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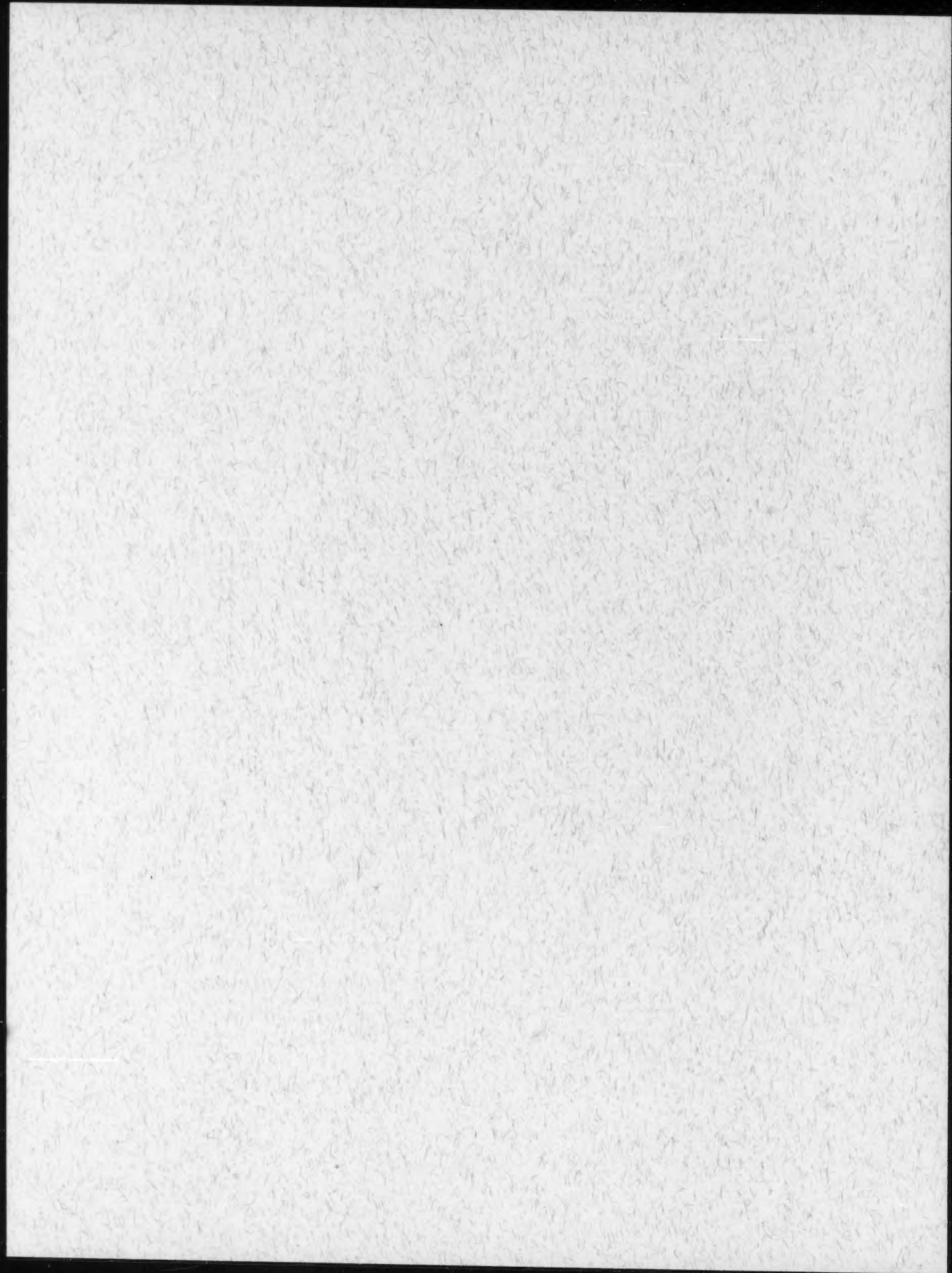
BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science
(IZVESTIYA AKADEMII NAUK SSSR)
(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION



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CONTENTS

	PAGE	RUSS. PAGE
Alumina Regions of Ternary Alumina-Silica Systems. Communication 3. The System $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$. <u>F. Ia. Galakhov</u>	513	529
Adsorption Properties of Carbon Adsorbents. Communication 2. Adsorption Properties of Active Carbons with Respect to Benzene and Nitrogen Vapors. <u>M. M. Dubinin and E. G. Zhukovskaya</u>	519	535
Radiation-Induced Reactions of Organic Substances. Communication 3. Transformations of Ethylene Produced by Fast Electrons. <u>B. M. Mikhailov, V. G. Kiselev and V. S. Bogdanov</u>	529	545
Physical and Chemical Properties of WS_2 Catalysts. Communication 2. Adsorption Properties of Mixed $\text{WS}_2 - \text{Clay}$ Catalysts. <u>S. M. Samollov and A. M. Rubinshtein</u>	534	550
Physical and Chemical Properties of WS_2 Catalysts. Communication 3. Phase Composition and Adsorption Properties of the Mixed Catalyst $\text{WS}_2 - \text{NiS} - \text{Al}_2\text{O}_3$. <u>S. M. Samollov and A. M. Rubinshtein</u>	540	557
Decomposition of Benzenediazonium Fluoroborate in Benzenesulfonic Esters and in Acetophenone. <u>L. G. Makarova and M. K. Matveeva</u>	548	565
Catalytic Dehydrogenation of n-Pentane at Various Temperatures. <u>E. A. Timofeeva and N. I. Shulkin</u>	552	570
Isomerization of Saturated Hydrocarbons. Communication 2. Isomeric Transformations of $\text{C}_{12} - \text{C}_{16}$ Paraffins. <u>Al. A. Petrov, S. R. Serglenko, A. L. Tsedilina, and M. P. Teterina</u>	557	575
Acetylene Derivatives. Communication 183. New Method for the Synthesis of 4-Piperidones; Action of Ammonia or Primary Amines on 1-Alkenyl 2-Dialkylaminoethyl Ketones. <u>I. N. Nazarov and E. A. Mistrukov</u>	565	584
Synthesis of Bifunctional Compounds from 2,5-Dimethylthiophene. <u>M. S. Kondakova and Ia. L. Gol'dfarb</u>	570	590
Synthesis of Polyalkylenearyls. Communication 5. Effect of Catalyst Concentration on the Course of the Copolycondensation of Benzene and Chlorobenzene with 1,2-Dichloroethane. <u>G. S. Kolesnikov, V. V. Korshak and A. P. Suprun</u>	579	600
Synthesis of Polyalkylenearyls. Communication 6. Effect of the Relative Amounts of Reactants on the Course of the Copolycondensation of Benzene and Chlorobenzene with 1,2-Dichloroethane. <u>G. S. Kolesnikov, V. V. Korshak and A. P. Suprun</u>	584	605

CONTENTS (continued)

	PAGE	RUSS. PAGE
Heterochain Polyesters. Communication 11. Chemical Degradation of Polyethylene Terephthalate. <u>V. V. Korshak, N. I. Bekasova and V. A. Zamiatina</u>	592	614
Organophosphorus Polymers. Communication 3. Polycondensation of Dichloro(p-chlorophenyl)phosphine with Bibenzyl. <u>V. V. Korshak, G. S. Kolesnikov and B. A. Zhubanov</u>	596	618
Brief Communications		
Catalytic Isomerization of Bicyclopentyl in Presence of Hydrogen Under Pressure. <u>N. I. Shulkin, M. I. Cherkashin and G. K. Galvoronskaia</u>	604	626
Tautomerism in Aprotic Media. Communication 1. Protolysis of Carboxylic Acids by Tris(p-dimethylaminophenyl)methanol. <u>M. I. Kabachnik and S. T. Ioffe</u>	607	628
Stereochemistry of Nucleophilic Addition at a Carbonyl Group. Reactions of 2-Methylcyclohexanone. <u>I. N. Nazarov, A. V. Akhrem and A. V. Kamernitskii</u>	611	631
Radiation-Induced Oxidation of Ferrous Iron in Aqueous Solutions. <u>B. V. Ershler and V. G. Firsov</u>	614	633
Introduction of Hydroxyacetone, Glycerol, and Dihydroxy-Carboxylic Side Chains into cis- and trans-Decahydronaphthalene Derivatives. <u>I. N. Nazarov, G. V. Aleksandrova and A. A. Akhrem</u>	616	634
Heterochain Polyesters. Communication 12. Terephthalic and Isophthalic Polyesters of Dihydric Phenols. <u>V. V. Korshak and S. V. Vinogradova</u>	619	637
Selectivity of Catalysts. Communication 2. Reduction of Mesityl Oxide Over Copper and Zinc-Copper Catalysts. <u>L. Kh. Freidlin, A. S. Sultanov and M. F. Abidova</u>	623	640
Transformations of Butene Under the Conditions of Synthesis from CO and H ₂ Over Fused Iron Catalysts. <u>Iu. B. Kriukov, A. N. Bashkirov, V. K. Butiugin, L. G. Liberov, and N. D. Stepanova</u>	626	642
Synthesis of Some (Trimethylsiloxy)titanium Compounds. <u>K. A. Andrianov and V. G. Dulova</u>	629	644
Chemical Nature of the Weak Linkages of the Cellulose Molecule. Communication 1. Effect of Carboxy Groups in the Cellulose Molecule on the Stability of the Glucosidic Link. <u>V. I. Ivanov and Z. I. Kuznetsova</u>	631	646
Reactions of Some Fluoro Olefins with Phenols. <u>I. L. Knunians and B. L. Diatkin</u>	634	648
Letters to the Editor		
New Method of Preparing Graft Copolymers. <u>V. V. Korshak and K. K. Mozgova</u>	637	651
Current Events		
Chemical Conference in the German Federal Republic in 1957. <u>A. D. Petrov, N. I. Shulkin</u>	638	652

ALUMINA REGIONS OF TERNARY ALUMINA-SILICA SYSTEMS

COMMUNICATION 3. THE SYSTEM $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$

F. Ia. Galakhov

The phase diagram of the system $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$, like those of other ternary alumina-silica systems, has not yet been studied in the alumina region. The investigation of this part of the phase diagram is of importance for the further development of our knowledge of heterogeneous equilibria in alumina-silica systems. In particular, the diagram is of practical importance in the establishment of the effect of additions of titanium dioxide on various refractory materials.

When heated to high temperatures (above 1000°), titanium dioxide gives up part of its oxygen and is converted into lower oxides. Ehrlich [1] investigated the system $\text{Ti} - \text{O}$; among products obtained by heating mixtures of Ti and TiO_2 he established by x-ray analysis the existence of four separate phases differing in the ratio $\text{Ti} : \text{O}$. Various papers [2-5] report the establishment of the existence of the compounds TiO , Ti_2O_3 , Ti_3O_5 , and describe their properties. On the basis of data in the literature, Devries and Roy [6] constructed a phase diagram of the system $\text{Ti} - \text{TiO}_2$. A peculiar feature of the system is the nonstoichiometric character of the compounds and the formation of solid solutions.

In the investigation of systems containing TiO_2 the main interest is concentrated on the extent of loss of oxygen from TiO_2 at the temperature of the experiment. Agamawi and White [7] give values of oxygen pressure below which TiO_2 is reduced to Ti_2O_3 ; at 1700° this pressure is $9.56 \cdot 10^{-8}$ atm. Hence, in the air at this temperature no reduction should occur. Nevertheless, the observed darkening of the color of a sample when heated to high temperatures indicates loss of oxygen. However, it was shown experimentally that the loss in weight due to the reduction of TiO_2 at 1550° is extremely small.

Lang, Fillmore, and Maxwell [8], who investigated the system $\text{BeO} - \text{Al}_2\text{O}_3 - \text{TiO}_2$ at temperatures ranging up to 1900° , state that the reduction of TiO_2 , which is indicated by a change in color to blue-black, must proceed only to a minute extent, because no proof of reduction could be found, either by petrographic methods or by x-ray analysis. They emphasize that a very small amount of Ti_2O_3 (less than 0.01%) has an exceptionally powerful coloring effect. Devries, Roy, and Osborn [9] studied the reduction of TiO_2 during the heating of mixtures of TiO_2 and SiO_2 by determining the loss in weight, and they concluded that almost the whole of the titanium is in the quadrivalent form. The highest temperature that they used was 1850° .

The first investigation of the system $\text{TiO}_2 - \text{Al}_2\text{O}_3$ was carried out by Rieke [10], who determined the melting points of cones prepared from mixtures of titanium dioxide and alumina. They found that the melting point fell as the cone changed in composition from pure alumina to about 60% TiO_2 . There was then a small maximum, and beyond this the melting point again fell continuously right to 100% TiO_2 . Wartenberg and Reusch [11] also determined the melting points of mixtures of titanium dioxide and alumina; their results were in good accord with the phase diagram later constructed for the system by Bunting [12]. According to Bunting, the system contains a compound $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$, m.p. 1860° , which forms eutectics with titanium dioxide (20% Al_2O_3) and with alumina (62% Al_2O_3). Later, Bron and Podnagin [13] found for this compound; refractive indices n_g 2.06 ± 0.005 , n_p 2.035 ± 0.005 ; birefringence 0.035-0.040; melting point 1890° . Lang, Fillmore, and Maxwell [8], who again verified the $\text{TiO}_2 - \text{Al}_2\text{O}_3$ diagram in connection with their investigation of the ternary system $\text{BeO} - \text{Al}_2\text{O}_3 - \text{TiO}_2$, obtained results in accord with those of Bunting. Fig. 1 gives the diagram of the system $\text{Al}_2\text{O}_3 - \text{TiO}_2$. These authors [8] found that $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ is dimorphous and has m.p. 1820° . The refractive indices are as follows:

$$\begin{aligned} \alpha\text{-Al}_2\text{O}_3 \cdot \text{TiO}_2: n_g 1,93; n_m 1,91; n_p 1,89 \\ \beta\text{-Al}_2\text{O}_3 \cdot \text{TiO}_2: n_g 1,99; n_m 1,97; n_p 1,95 \end{aligned}$$

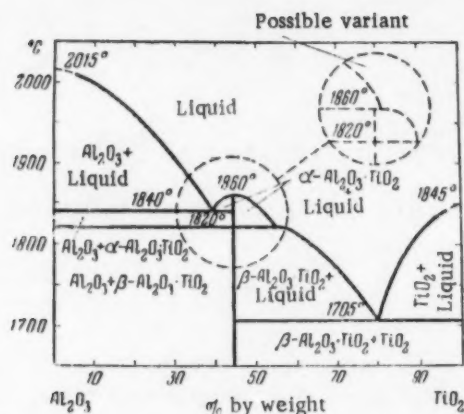


Fig. 1. Phase diagram of the system $\text{Al}_2\text{O}_3 - \text{TiO}_2$ according to Lang, Fillmore, and Maxwell

By determining the melting points of cones prepared from mixtures of a kaolin and titanium dioxide, Riecke [10] initiated the study of the ternary system $\text{TiO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$. The melting point was at its lowest and was approximately constant (about 1530°) for mixtures containing from 30 to 70% TiO_2 . Mackenzle [14], who determined the melting points of rods consisting of silica with additions of up to 6% Al_2O_3 , showed that the depression of melting point produced by titanium dioxide is about one-half of that produced by alumina.

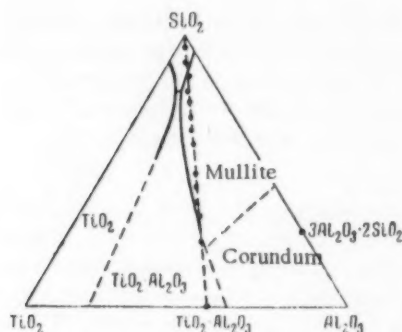


Fig. 2. Phase diagram of the system $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ according to Agamawi and White.

boundary was the source of their lack of success in finding corundum and determining the invariant point. As will be seen from the results of the present work, the actual position of this point is rather distant from the area in which Agamawi and White were seeking it.

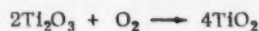
EXPERIMENTAL

Determination of the Extent of the Reduction of TiO_2 . It is evident from the literature on systems containing titanium dioxide that investigators have not taken the reduction of quadrivalent titanium into account in the construction of phase diagrams because only an extremely small proportion of the titanium is found to be in a lower valence state.

In the present work samples were prepared by the fusion of mixtures in the electric arc. The fused preparations were almost black, which could be due to the reduction of titanium under the action of the high temperature

Agamawi and White [7] made a detailed investigation of the system $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$. They made a preliminary investigation by the method of the melting of cones and then studied equilibrium by the quenching method. On the basis of the results they constructed equilibrium diagrams for the line $\text{SiO}_2 - \text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ and for the ternary system (Fig. 2). The system has three invariant points, but the authors did not succeed in establishing the composition at one of these. This was the point for the fields of mullite, corundum, and $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$; the authors sought for it in the region of the possible intersection of the boundary of mullite-aluminum titanate with that of mullite-corundum, since they held the view that the second boundary originates in the peritectic point of the alumina-silica system, as established by Bowen and Greig [15]. Their incorrect view on the position of the mullite-corundum

of the arc and of a reducing atmosphere. In order to determine the extent of the reduction, a weighed sample of composition 37% TiO_2 , 51% Al_2O_3 , and 12% SiO_2 after fusion in the arc was heated in a tube furnace in a platinum boat at 600-900° for five hours with periodic cooling and weighing. The color of the sample changed to white; its weight increased by 0.05%. On the basis of the reaction



this increase in weight corresponds to a content of 0.52% Ti_2O_3 in the sample or 1.4% on the TiO_2 content of the sample. The other samples used in the study of the ternary system contained less than 37% TiO_2 and their Ti_2O_3 contents were therefore less than 0.5%. Such amounts of Ti_2O_3 could scarcely affect the results of the experiments to such an extent as to alter the phase diagram appreciably. The reduction of titanium dioxide during annealing is unlikely to occur because the heating was carried out in an inert gas and lasted for about 30 seconds; only at temperatures below 1700° was the time lengthened to 3 minutes.

The procedure that we used for the study of heterogeneous equilibria was described in previous communications [16].

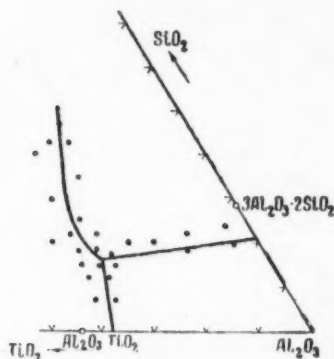


Fig. 3. Alumina region of the system $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ (the points indicate the compositions studied).

investigation, were consistent within less than 1%, which indicates satisfactory agreement between the results. The direction of the boundary between the corundum and aluminum titanate fields is in accord with the eutectic point of the binary system $\text{TiO}_2 - \text{Al}_2\text{O}_3$, as established by the work of other authors [8, 11, 12].

In the studied region of the ternary system $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$, we established the existence of one invariant point: composition 32% TiO_2 , 52% Al_2O_3 , 16% SiO_2 ; m.p. 1710°. This point is common to the corundum, mullite, and aluminum titanate fields, and it is of the reaction type since it falls outside the field of the phase triangle of these compounds. The reaction character of this point is confirmed by the course of the crystallization of a test sample taken in the corundum field and having the composition 30% TiO_2 , 55% Al_2O_3 , 15% SiO_2 (see table). At 1750° corundum crystallizes from the melt, and at 1700° aluminum titanate and mullite separate simultaneously, whereas corundum is absent.

As noted above in the literature review, the position found for the invariant point of the corundum, mullite, and aluminum titanate fields differs from that in which Agamawi and White [7] tried to find it. They considered that this point should lie at a level of about 25% SiO_2 . They had to take account of the possible direction of the mullite-corundum boundary and, being convinced that this boundary passes from the reaction point of the binary system alumina-silica established by Bowen and Greig [15], they were probably unable to admit the possibility of a boundary line of high slope.

In Fig. 4 we give the phase diagram of the ternary system $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ with isotherms; in this diagram the data of Agamawi and White and of the present work are combined. The diagram includes the

In the alumina region of the ternary system we established the boundaries between the fields of corundum, mullite, and aluminum titanate $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$. The positions of the boundaries were established from points representing definite compositions, which are given in the table together with the results of their investigation. Fig. 3. represents this region of the ternary diagram with the compositions studied and the established positions of the boundary lines. The boundary between the corundum and mullite fields was placed in accordance with the eutectic that we found in the system alumina-silica. The position of the boundary between the mullite and aluminum titanate fields was established up to a composition for which the SiO_2 content was 47%. Beyond this the position of the boundary has been determined by Agamawi and White [7], who investigated compositions of 50% and more SiO_2 . The two branches of the boundary, one of which was established by Agamawi and White and the other by the present in-

TABLE
Results of the Quenching of Samples in the System $\text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$

Composition (% by weight)			Tempera- ture (°C)	Time	Phases*
TiO ₂	Al ₂ O ₃	SiO ₂			

Boundary between the corundum and mullite field

Corundum fields					
30	55	15	1800	15 sec	glass
			1750	15 "	K + glass
			1700	15 "	T + M + glass
15	67	18	1800	10 "	K + glass
			1750	10 "	K + M + glass
5	75	20	1850	15 "	K + glass

Mullite field					
30	53	17	1750	15 "	glass
			1720	15 "	glass
			1680	15 "	M + T + glass
25	55	20	1800	10 "	glass
			1750	10 "	M + glass
20	60	20	1800	15 "	glass
			1750	15 "	M + glass
13	65	22	1850	10 "	glass
			1800	10 "	M + glass
5	72	23	1850	15 "	M + glass (very little)

Boundary between the mullite and aluminum titanate fields

Mullite field					
25	28	47	1600	3 min.	glass
			1550	3 "	M + T + glass (lies on the boundary)
25	32	43	1650	3 "	glass
			1600	3 "	M + glass
			1550	3 "	M + T + glass
27	38	35	1700	3 "	glass
			1650	3 "	M + glass
32	43	25	1650	1 "	glass
			1600	1 "	M + glass
32	50	18	1700	30 sec	glass
			1680	30 "	M + glass
			1650	30 "	M + T + glass

Aluminum titanate field

29	28	43	1550	3 min.	glass
			1530	3 "	T + glass
			1500	3 "	T + M + glass
33	27	40	1600	3 "	glass
			1550	3 "	T + glass
35	35	30	1640	2 "	glass
			1590	2 "	T + glass
35	43	22	1700	10 sec	glass
			1680	10 "	T + glass
			1650	10 "	T + M + glass
40	40	20	1700	20 "	glass
			1650	20 "	T + glass
36	46	18	1700	1 min.	glass
			1650	1 "	T + glass
37	48	15	1750	10 sec	glass
			1700	10 "	T + glass

* K = corundum; M = mullite; T = aluminum titanate.

TABLE (cont'd.)

Composition (% by weight)			Temperature (°C)	Time	Phases*
TiO ₂	Al ₂ O ₃	SiO ₂			
Boundary between the corundum and aluminum titanate fields					
Corundum field					
30	35	15	1800	15 sec	glass
			1750	15 »	K + glass
			1700	15 »	T + M + glass
33	55	12	1750	10 »	glass
			1700	10 »	K + T + glass (lies close to the boundary
34	59	7	1770	30 »	K + glass
Al ₂ O ₃ -TiO ₂ Field					
33	52	15	1750	10 sec	glass
			1700	10 »	T + K + glass (lies close to the boundary)
37	51	12	1750	10 »	T + glass
			1700	10 »	T + glass
38	55	7	1770	30 »	T + glass

aluminum titanate field: this is divided into two parts by the 1820° isotherm; they correspond to the high-temperature α - and low-temperature β -modifications of aluminum titanate, in accordance with the data of Lang,

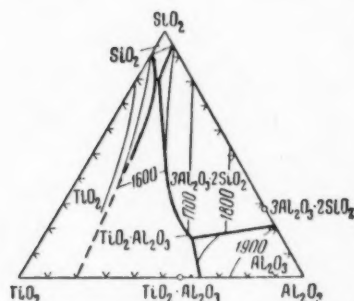


Fig. 4. Phase diagram of the system TiO_2 - Al_2O_3 - SiO_2 , as given by Agamawi and White and supplemented by the results of the present work (boundaries in the alumina region).

Fillmore, and Maxwell [8]. These authors suggest the possibility of incongruent melting of aluminum titanate, though they themselves note much evidence for melting without decomposition. The presence of an aluminum titanate field in the ternary system that is directly accessible from the figurative point for $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ is further evidence in favor of the congruence of the melting of aluminum titanate.

We are greatly indebted to the director of the Physicochemical Laboratory of the Institute of Silicate Chemistry of the Academy of Sciences of the USSR, N. A. Toropov, for advice and for constant interest in our work.

SUMMARY

1. The phase diagram was constructed for the alumina region of the ternary system TiO_2 - Al_2O_3 - SiO_2 .
2. The direction of the boundary between the corundum and mullite fields is in accord with the position of the eutectic point which we found previously in the alumina-silica system.
3. The position of the invariant point for the corundum, mullite, and aluminum titanate fields differs greatly from that suggested by Agamawi and White. These authors were unable to find this point because they took the incorrect diagram of Bowen and Greig as their basis.
4. Our results confirm the view that aluminum titanate has a congruent melting point.

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ADSORPTION PROPERTIES OF CARBON ADSORBENTS

COMMUNICATION 2. ADSORPTION PROPERTIES OF ACTIVE CARBONS WITH RESPECT TO BENZENE AND NITROGEN VAPORS

M. M. Dubinin and E. G. Zhukovskaya

Nitrogen and benzene vapors are used as standard substances in the investigation and evaluation of the adsorption properties of active carbons. In other countries nitrogen is generally used, adsorption isotherms being determined at -195° over a wide range of equilibrium pressures. In the USSR the preferred standard vapor for this purpose is that of benzene, which is used at 20° . The correlation of the adsorption properties of active carbons with respect to these two standard vapors has not yet been established, and the present investigation is devoted to this task.

Owing to the nonpolarity of carbon, the physical adsorption of gases and vapors arises solely from dispersion forces; the part played by electrostatic components of the interaction is extremely small. In the general case of porous carbon adsorbents such as active carbons, we meet adsorbents that have energetically heterogeneous surfaces. We may name at least two causes for such heterogeneity: the first is associated with the disorderly disposition of elementary carbon crystallites at the adsorbent surface, which acquires a sort of mosaic structure formed by the various crystal planes. The second cause is associated with the enhanced adsorption potentials in the fine pores of active carbons; these result from the superposition of the fields of the opposite walls of pores that are comparable in size with the molecules being adsorbed. A typical manifestation of energetic heterogeneity of the surface is the sharp fall in differential heat of adsorption with increase in coverage.

For active carbons with such a marked energetic heterogeneity of surface the theory of physical adsorption based on the assumption of a homogeneous surface (see e.g. [1]) is not applicable. The theory that is most closely applicable in the description of the experimental data is the potential theory of adsorption proposed by Polanyi [2, 3], developed further in our investigations, and expounded in a generalized form in [4]. The analysis of our experimental results will therefore be based on the potential theory of adsorption.

EXPERIMENTAL

As objects for investigation we used typical samples of active carbons of the first structural type [5], for which the effect of enhanced adsorption potentials in micropores consisted in the whole of the practically realizable range of values. All carbon samples were obtained under laboratory conditions by the activation of previously carbonized grains or granules with carbon dioxide or steam in a rotating furnace at a constant temperature in the range $850-950^{\circ}$. The active carbons differed with respect to the carbonized material used and to the combustion loss during activation. We now give information concerning the samples of active carbons.

1) AU 3 and 7. These were prepared according to [6] from carbonized sucrose by activation with carbon dioxide at 850° to combustion losses of about 10 and 40%.

2) AU 2. This was prepared according to [7, 8] from briquetted polyvinylidene chloride powder that had been heated slowly in a vacuum until the temperature reached 700° ; the carbonized product was activated with carbon dioxide with only a small combustion loss.

3) AU 1, 4, 5, and 6. Granulated active carbons based on coals and wood resin. They were activated with carbon dioxide or steam at about 950° .

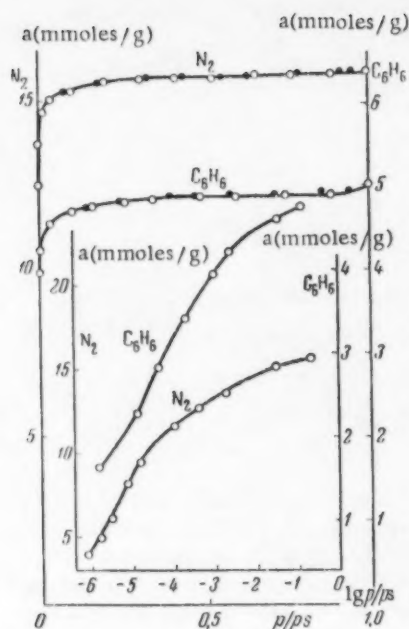


Fig. 1. Sorption and desorption isotherms for benzene vapor at 20° and nitrogen vapor at -195° on AU 2. The adsorption scale for nitrogen is on the left and that for benzene on the right. In Figures 1-3 the desorption points are indicated by black circles.

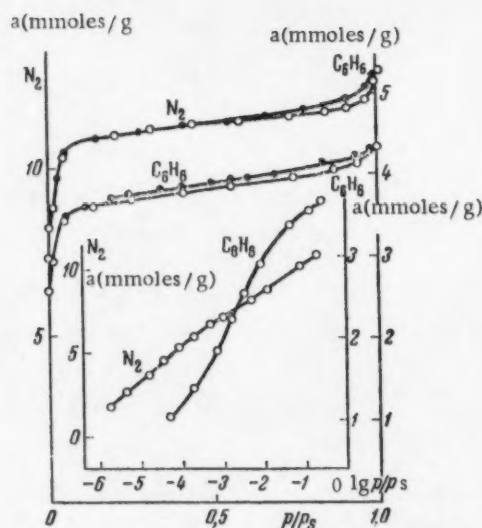


Fig. 2. Sorption and desorption isotherms for benzene vapor at 20° and nitrogen vapor at -195° on AU 8.

The sorption and desorption isotherms for benzene vapor at 20° and nitrogen vapor at -195° were investigated by the vacuum sorption-balance method. The apparatus and technique are described in detail in [9]. The samples of active carbons were ground, and the fraction of grains held during sieving between sieves having circular holes of diameter 0.5 and 1.0 mm was used in the experiments. The weight of the carbon

sample taken was 90-140 mg. Preliminary evacuation of the carbons was carried out at 450° for 8 hours until the residual pressure was below 10^{-6} mm. In some cases experiments with benzene and nitrogen were carried out on the same carbon sample. The measurement of the adsorption isotherm was generally repeated at least twice.

Special attention was paid to the attainment of a state of sorption equilibrium. In the adsorption region of the isotherms equilibrium was generally established in 1-1.5 hours, and the adsorption and desorption points could be fitted very well to the same curve. In the capillary-condensation region of the isotherms equilibrium was attained much more slowly, particularly during sorption (1.5-4 hours).

By way of examples, in Figures 1-3 we give characteristic sorption and desorption isotherms for benzene and nitrogen vapors. In each figure the initial parts of the isotherms are given also on a semilogarithmic scale. The sorption and desorption isotherms for AU 2, 3, and 7 are reversible over the whole range of equilibrium pressures studied, and in general character they are analogous to the isotherms for AU 2 represented in Fig. 1. At high relative pressures the hysteresis region is absent or cannot be resolved within the limits of the accuracy of measurement. The isotherms for AU 8 and 9 are characterized by a reversible adsorption up to the start of the hysteresis loop and by noncoincidence of the sorption and desorption branches of the isotherm at high relative pressures. The hysteresis loops rise gently in accord with the relative small volume of the pores of the carbon in which the capillary condensation occurs (see Fig. 2 for AU 8). The sorption and desorption isotherms for AU 1, 4, 5, and 6, a typical example of which is the isotherm for AU 5 (Fig. 3), are distinguished by the steeper rise of the sorption and desorption branches in the hysteresis region. For these carbons the volume of pores filled as a result of capillary condensation is considerably greater, particularly at pressure approaching the saturation value. The presence and character of the hysteresis loop on sorption isotherms depend essentially on the extent of the transitional pores of the active carbons and their distribution with respect to pore size.

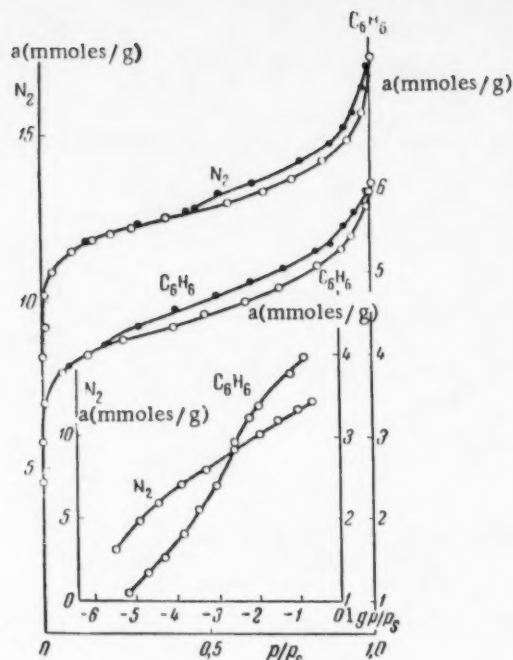


Fig. 3. Sorption and desorption isotherms for benzene vapor at 20° and nitrogen vapor at -195° on AU 5.

Type 3 include those for benzene and nitrogen vapors on AU 1, 4, 5, 6, 8, and 9, which have marked hysteresis loops. The sorption isotherms without hysteresis loops for AU 3 and 7 belong to Type 1. For AU 2 the nitrogen isotherm belongs to Type 1 and the benzene isotherm to Type 2 (which was found for only one carbon-vapor system).

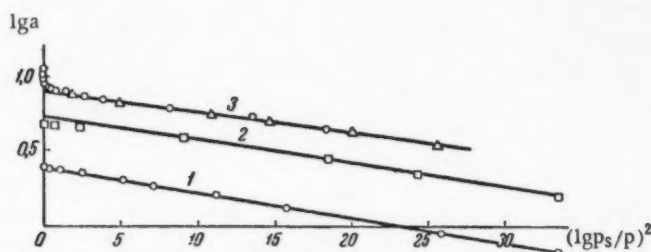


Fig. 4. Adsorption isotherms for benzene and nitrogen vapors in the linear form (Equation (2): 1) benzene, 20°, AU 3; 2) benzene, 20°, AU 2; 3) nitrogen, -195°, AU 4.

Tables 1 and 2 give constants of adsorption isotherm equations (2) for all active carbon samples studied, and the ranges of relative pressures in which the equation expresses the experimental results are indicated. The tables give values of relative pressure $(p/p_s)_0$ for the points at the start of hysteresis and the corresponding volumes of sorbed vapor in the liquid state, which may be conditionally treated as the volumes of micropores of the carbons v_{mi} . The limiting sorption volumes may be denoted by v_s

$$v_s = a_s v, \quad (5)$$

For the adsorption branches of the adsorption isotherms of the active carbons studied, the following equation applies over a wide range of equilibrium pressures:

$$a = \frac{W_0}{v} e^{-B \frac{T^2}{\beta^2} (\lg p_s/p)^2}, \quad (1)$$

In which W_0 is the limiting volume of adsorption space, B is a constant characterizing the steepness of the isotherm; v is the volume of a millimole of liquefied vapor at the temperature T of the experiment, and β is the affinity coefficient of the characteristic curve [5]. In the linear form the equation to the adsorption isotherm (1) has the form:

$$\lg a = C - D (\lg p_s/p)^2, \quad (2)$$

$$C = \lg \frac{W_0}{v}, \quad (3)$$

$$D = 0.434 B \frac{T^2}{\beta^2}. \quad (4)$$

Fig. 4 shows typical adsorption isotherms in the linear form for benzene and nitrogen vapors; they differ in the way the experimental points depart from the straight line at high relative pressures beyond the range of applicability of the equation. Sorption isotherms of

in which a_s is the limiting sorption at $p/p_s = 1$, and in accordance with [10] the difference

$$v_l = v_s - v_{ml} \quad (6)$$

can be conditionally identified with the volume of intermediate pores.

In the tables the active carbons are arranged in order of increasing values of the constant D of Equation (2) for benzene, i.e., in accordance with (4), the constant B of Equation (1). This sequence of carbons is in the main preserved in Table 2 for nitrogen.

TABLE 1
Sorption of Benzene Vapor at 20°

AU	C	D · 10 ³	Range of p/p _s in which equation applicable	Point of start of hysteresis		v _l (cc/g)	s _l (sq. m/g)	v _s (cc/g)
				(p/p _s) ₀	v _{ml} (cc/g)			
1	0,320	1,43	3 · 10 ⁻⁶ —1 · 10 ⁻¹	0,175	0,192	0,076	32,3	0,268
2	0,728	1,52	1,2 · 10 ⁻⁶ —4 · 10 ⁻³	—	0,426	0,022	—	0,448
3	0,387	1,66	1,2 · 10 ⁻⁶ —1,5 · 10 ⁻¹	—	0,211	0,007	—	0,218
4	0,450	2,12	2 · 10 ⁻³ —1,3 · 10 ⁻¹	0,175	0,249	0,115	67,1	0,364
5	0,613	2,35	2,5 · 10 ⁻⁵ —1 · 10 ⁻¹	0,175	0,360	0,167	80,7	0,527
6	0,540	2,62	2,5 · 10 ⁻⁵ —1,5 · 10 ⁻¹	0,180	0,284	0,178	98,9	0,462
7	0,757	2,77	1 · 10 ⁻⁵ —4 · 10 ⁻³	—	0,505	0,015	—	0,520
8	0,610	3,16	2 · 10 ⁻⁵ —1,5 · 10 ⁻¹	0,175	0,346	0,098	33,9	0,444
9	0,570	3,72	3 · 10 ⁻⁵ —1 · 10 ⁻¹	0,170	0,348	0,090	45,3	0,438

TABLE 2
Sorption of Nitrogen Vapor at -195°

AU	C	D · 10 ³	Range of p/p _s in which equation applicable	Point of start of hysteresis		v _l (cc/g)	s _l (sq. m/g)	v _s (cc/g)
				(p/p _s) ₀	v _{ml} (cc/g)			
1	0,792	1,08	1 · 10 ⁻⁵ —1 · 10 ⁻¹	0,47	0,233	0,040	23,2	0,273
2	1,210	0,933	2 · 10 ⁻⁵ —1,5 · 10 ⁻¹	—	0,548	0,005	—	0,553
3	0,880	1,08	8 · 10 ⁻⁶ —1,5 · 10 ⁻¹	—	0,270	0,002	—	0,272
4	0,890	1,27	1,5 · 10 ⁻⁵ —1 · 10 ⁻¹	0,45	0,302	0,072	48,1	0,374
5	1,075	1,59	1 · 10 ⁻⁵ —1 · 10 ⁻¹	0,45	0,445	0,141	65,2	0,586
6	0,953	1,67	2 · 10 ⁻⁵ —7 · 10 ⁻²	0,44	0,354	0,112	83,3	0,466
7	1,163	1,78	1 · 10 ⁻⁵ —1,5 · 10 ⁻¹	—	0,512	0,008	—	0,520
8	1,035	2,03	1 · 10 ⁻⁵ —1,5 · 10 ⁻¹	0,50	0,398	0,087	21,2	0,465
9	0,978	2,28	2 · 10 ⁻⁵ —7 · 10 ⁻²	0,40	0,369	0,073	37,2	0,442

From the experimental results we may conclude that Equation (1) for the adsorption isotherm is applicable over a wide range of relative pressures.

The relative pressures at the points of the start of hysteresis for the various carbons fall within narrow ranges of values: 0.170-0.180 for benzene and 0.40-0.50 for nitrogen. The volumes of micropores for AU 2, 3, and 7 were calculated from the sorption isotherms for mean values of these quantities, i.e. $(p/p_s)_0 = 0.175$ for benzene and $(p/p_s)_0 = 0.45$ for nitrogen. The volumes of micropores and intermediate pores given in Tables 1 and 2 vary considerably for the active carbon samples studied. The limiting values of the sorption of benzene and nitrogen vapors for AU 1-5, which stand at the beginning of the series of carbons, cannot be regarded as identical either.

DISCUSSION OF RESULTS

1. From the constants C_A for nitrogen and C_B for benzene in the adsorption isotherm equations (2) we

calculated the limiting volumes of the adsorption spaces W_0^A and W_0^B given in Table 3. In the same Table 3 we give the constants B of the equation of the adsorption isotherm of benzene, taken as a standard vapor ($\beta = 1$), and the affinity coefficients β of the characteristic curves for nitrogen calculated from values of the constants D_A and D_B for nitrogen and benzene taken from Tables 1 and 2. The calculation was made by means of an equation derived from (4) for the given experimental conditions:

$$\beta = 0,264 \sqrt{\frac{D_B}{D_A}}. \quad (7)$$

According to Table 3, for the samples of active carbons studied, the constants B fill the whole range of values known for adsorbents of the first structural type in an almost regular manner. With the exception of the value for AU 1, the affinity coefficients β do not show any substantial variation, and as a mean value we may take $\beta = 0.33 \pm 0.01$, which is almost identical with the ratio of parachors of nitrogen P_A and benzene P_B calculated from the increments given by Sugden [11]:

$$\beta = \frac{P_A}{P_B} = \frac{70,0}{207,1} = 0,338. \quad (8)$$

The expression (8) was proposed by Vas'kovskii [12] in the development of an approximate method of calculating affinity coefficients given by Dubinin and Timofeev [13]. The agreement between experimental and calculated values of affinity coefficients enables us to conclude that dispersion forces play the determining part in the adsorption processes of nitrogen and benzene vapors.

TABLE 3
Constants of Adsorption Isotherm Equations and Affinity Coefficients of Characteristic Curves

AU	$B \cdot 10^4$	β	Nitro- gen W_0^A	Ben- zene W_0^B	$\frac{W_0^A}{W_0^B}$
1	0,382	[0,303]	0,216	0,186	1,16
2	0,407	0,336	0,568	0,475	1,20
3	0,445	0,328	0,264	0,217	1,21
4	0,568	0,340	0,270	0,251	1,08
5	0,629	0,320	0,414	0,364	1,14
6	0,702	0,330	0,342	0,308	1,01
7	0,742	0,328	0,506	0,508	1,00
8	0,910	0,340	0,378	0,361	1,05
9	1,00	0,336	0,331	0,330	1,01

TABLE 4
Volumes of Pores of Active Carbons Filled in the Sorption of Nitrogen Vapor, but Inaccessible to Benzene Molecules

AU	$W_0^A - W_0^B$ (cc/g)	$V_s^A - V_s^B$ (cc/g)	Mean value (cc/g)
1	0,030	0,005	0,017
2	0,093	0,105	0,099
3	0,047	0,054	0,050
4	0,019	0,010	0,015
5	0,050	0,059	0,055
6	0,004	0,004	0,004
7	0	0	0
8	0,017	0,021	0,019
9	0,001	0,004	0,002

The limiting volumes of adsorption space for AU 1-5 calculated from experiments with nitrogen are substantially greater than those determined with the aid of benzene. Since active carbons associated with low values of B contain fine micropores, it is natural to attribute the difference in the values of W_0^A and W_0^B to ultraporosity, i.e. inaccessibility of part of the finest micropores to the larger benzene molecules. However, in such a case the difference between the limiting values of adsorption space should in principle coincide with the difference between the limiting sorption volumes V_s for every carbon. The values of these differences are compared in Table 4.

If we neglect the exceptional results for AU 1, then for the remaining carbons the differences in limiting values of adsorption space W_0 and in limiting sorption volumes V_s determined by independent methods are fairly close, particularly if we consider the difficulty of measuring V_s exactly. For each carbon the difference $\Delta_1 = W_0^A - W_0^B$ can be regarded as a correction for the ultraporosity effect, i.e. as the volume of micropores

filled in the adsorption of nitrogen molecules, but inaccessible for the larger molecules of benzene. Hence, for each carbon sample the difference between the values of W_0 or v_s in experiments with nitrogen and benzene vapors is due to the ultraporosity effect. It should be noted that, as a result of certain features (not given here) of the preparation of AU 8, the presence of a certain volume of extremely fine micropores in this sample would be expected.

2. For the benzene adsorption isotherms the mean value of the equilibrium relative pressure $(p/p_s)_0$ at the start of hysteresis is 0.175, and for the nitrogen isotherms it is 0.45. If we apply Kelvin's equation to these substances, i.e. for the given experimental conditions:

$$r_k^B = \frac{9.15}{\lg p_s / p} \cdot 10^{-8} \text{ cm} \quad (9)$$

$$r_k^A = \frac{4.14}{\lg p_s / p} \cdot 10^{-8} \text{ cm} \quad (10)$$

then from the values of $(p/p_s)_0$ it is easy to calculate the effective Kelvin radii r_k^B and r_k^A of the free spaces between adsorption films, the values obtained being $(12.1 \pm 0.2) \cdot 10^{-8} \text{ cm}$ for experiments with benzene and $(11.9 \pm 1.7) \cdot 10^{-8} \text{ cm}$ for experiments with nitrogen. Hence, the starting points of irreversible capillary condensation of benzene and nitrogen vapors, i.e. the points representing the start of hysteresis on the adsorption isotherms, correspond to almost identical radii of free space between adsorption films in the pores of active carbons. It will be clear that in this case we are considering model sorbents having cylindrical or uniformly conical pores corresponding to the carbon samples 1, 4, 5, 6, 8, and 9 [14].

From the adsorption isotherms of benzene vapor at 20° and nitrogen vapor at -195° on nonporous carbon black vacuum-treated at 950° and having a known specific surface s , we may determine mean statistical thicknesses of adsorption layers l from the values of adsorption a_0 (mmoles/g) at equilibrium pressures $(p/p_s)_0$ corresponding to the starting points of hysteresis on the isotherms of active carbons:

$$l = \frac{a_0 v}{s}, \quad (11)$$

in which v is the volume of one millimole of liquefied vapor at the temperature of the experiment. Making use of experimental data in [15,16], we obtained, for benzene vapor at 20° , $p/p_s = 0.175$ and $l_B = 3.7 \cdot 10^{-8} \text{ cm}$ and, for nitrogen vapor at -195° , $p/p_s = 0.45$ and $l_A = 5.2 \cdot 10^{-8} \text{ cm}$. The effective radii of pores of active carbons

$$r = r_k + l \quad (12)$$

for the start of capillary condensation will be $r^B = 1.58 \cdot 10^{-7} \text{ cm}$ for benzene vapor and $r^A = 1.73 \cdot 10^{-7} \text{ cm}$ for nitrogen vapor. Hence, the points for the start of hysteresis on the sorption isotherms of benzene and nitrogen correspond to different volumes of pores of the carbon filled with liquefied vapors of these substances as a result of adsorption and capillary condensation. This, as well as the ultraporosity effect, forms a cause of the difference in the volumes of micropores of carbons v_{mi}^B and v_{mi}^A , as determined from the points for the start of hysteresis on the sorption isotherms of benzene and nitrogen vapors (Tables 1 and 2).

The condition of equal volumetric filling of the pores of an active carbon with benzene and nitrogen as a result of adsorption and capillary condensation will correspond to a high relative pressure of benzene vapor $(p/p_s)_1$, for which $r_k^B + l_B = 1.73 \cdot 10^{-7} \text{ cm}$. By determining from this the Kelvin radius r_k^B , we readily find from Equation (10) that $(p/p_s)_1 = 0.21$. For this pressure the sorption volume of benzene W_B corresponding to the desorption branch of the isotherm will be equal to the sorption volume of nitrogen W_A , with the condition that the latter quantity includes only the volume of pores of the carbon accessible both to nitrogen and to benzene molecules. The value of this correction Δ_2 , expressed in volumes of liquid, will be

$$\Delta_2 = (a_1 - a_0) v, \quad (13)$$

in which a_1 is the sorption of benzene vapor according to the desorption branch of the isotherm at equilibrium pressure $(p/p_s)_1 = 0.21$, and a_0 is the sorption for the start of hysteresis, i.e. for $(p/p_s)_0 = 0.175$.

A third cause of the difference between the volumes v_{ml}^B and v_{ml}^A lies in the unequal volumes of multi-molecular adsorption layers of benzene and nitrogen on the surface s_i of the larger pores (intermediate pores), which are not volumetrically filled at equilibrium pressures corresponding to the points for the start of hysteresis on the sorption isotherms. As the thickness of the adsorption layer of nitrogen $l_A = 5.2 \cdot 10^{-8}$ cm is greater than the thickness of the adsorption layer of benzene $l_B = 3.7 \cdot 10^{-8}$ cm, the correction for the difference in volumes will be expressed by

$$\Delta_3 = (l_A - l_B) \bar{s}_i = 1.5 \cdot 10^{-8} \cdot \bar{s}_i, \quad (14)$$

in which \bar{s}_i is the specific surface of intermediate pores, which can be estimated from the surface area of the adsorption film in intermediate pores in accordance with [17]. Tables 1 and 2 give specific surfaces of intermediate pores s_i calculated in this way. Calculation from the desorption branches of benzene isotherms gives values of surfaces that are 20-40% higher than those calculated from nitrogen isotherms. The cause of such a great discrepancy lies in the inadequately accurate graphical determination of the positions of the points for the start of hysteresis on the isotherms. It is possible that the condition $s_i^B = s_i^A$ would facilitate the solution of this problem. In Equation (14) we used mean values of specific surfaces $\bar{s}_i = \frac{1}{2} (s_i^B + s_i^A)$.

TABLE 5
Comparison of Volumes of Micropores of Active Carbons Determined from Points at the Start of Hysteresis on the Sorption Isotherms of Nitrogen and Benzene Vapors

AU	Nitrogen v_{ml}^A	Δ_1	Δ_2	Δ_3	$\Sigma \Delta$	$v_{ml}^A - \Sigma \Delta$	Benzene v_{ml}^B
1	0,238	0,030	0,006	0,004	0,040	0,193	0,192
2	0,548	0,093	0	0	0,093	0,455	0,426
3	0,270	0,047	0	0	0,047	0,223	0,211
4	0,302	0,019	0,011	0,009	0,039	0,263	0,249
5	0,445	0,050	0,007	0,011	0,068	0,377	0,360
6	0,354	0,004	0,027	0,014	0,045	0,309	0,284
7	0,512	0	0	0	0	0,512	0,505
8	0,398	0,017	0,006	0,004	0,027	0,371	0,346
9	0,369	0,001	0,009	0,006	0,016	0,353	0,348

TABLE 6
Volumes of Micropores and Intermediate Pores of Active Carbons (cc/g)

AU	v_{ml}^B	W_0^B	$v_s^B - W_0^B$	$v_s^A - W_0^A$
1	0,19	0,19	0,08	0,06
2	0,43	0,47	—	—
3	0,21	0,22	0,00	0,01
4	0,25	0,25	0,11	0,10
5	0,36	0,36	0,16	0,17
6	0,28	0,31	0,15	0,15
7	0,51	0,51	0,00	0,01
8	0,35	0,36	0,08	0,09
9	0,35	0,33	0,11	0,11

In Table 5 we compare sorption volumes for points at the start of hysteresis on the sorption isotherms of nitrogen and benzene vapors, which are referred to conditionally as the volumes of micropores v_{ml}^A and v_{ml}^B for different active carbons. It will be seen from Table 5 that the introduction of all the corrections enumerated above brings the values for the sorption volumes of nitrogen at the start of hysteresis (penultimate column of Table 5) closer to the corresponding sorption volumes of benzene, agreement being almost exact in some cases. Hence, in the general case the sorption volumes of different vapors at the start of the hysteresis loop cannot be taken as the volumes of the micropores of the active carbons. This conclusion follows quite clearly from our experiments on the sorption of nitrogen and benzene vapors on various active carbons.

3. Physical adsorption, due to dispersion forces, in active carbons of the first structural type occurs in the adsorption space limited by the walls of the micropores. From this point of view, the limiting volumes of the adsorption space should coincide with the volumes of the micropores of the active carbons, which are filled completely as a result of the coming together of the adsorption layers on opposite walls of the pores in the primary

adsorption process before the start of capillary condensation of vapor in the larger intermediate pores. The difference in limiting volumes of adsorption space W_0 calculated from experiments with different vapors on a given sample of active carbon can be due only to the ultraporosity effect. The adsorption of vapor on the surface of the coarser, e.g. intermediate, pores does not affect W_0 appreciably [18]. For organic vapors on commercial active carbons the limiting volumes of adsorption space are constant within less than 7% [19]. All this gives us grounds for regarding the limiting volumes of adsorption space as the most rational measure of the volumes of the micropores of active carbons.

In the investigations of recent years it has been established in detail that the sorption volumes of methanol and benzene vapors express the volumes of the micropores of active carbons [10,20,21]. Table 6 gives a comparison of the volumes of the micropores of the investigated active carbons determined in this way with the limiting volumes of adsorption space given by experiments on the adsorption of benzene vapor.

Table 6 shows that the limiting volumes of adsorption space W_0^B are almost the same as the volumes of micropores v_{mi}^B determined by the old, more approximate method. The small discrepancy for AU 2 is associated with the peculiar character of the departure of the points from a straight line at high relative pressures in the graph of Fig. 4. If we regard the limiting volumes of adsorption space W_0 as the more correct values of volumes of micropores of active carbons of the first structural type, then the differences between limiting sorption volumes v_s and the volumes of micropores will express the volume of pores of active carbons in which capillary condensation of vapor occurs, i.e. the volume of intermediate pores v_i :

$$v_i = v_s - W_0 \quad (15)$$

It follows from the experimental data in Table 6 that the volumes of intermediate pores calculated from Equation (15) for the adsorption of benzene and nitrogen are almost constant quantities for each sample of active carbon, which cannot at all be said of the values of v_i found by the old method from Equation (6) for the adsorption of benzene and nitrogen (see Tables 1 and 2). For active carbons having extremely fine pores accessible only to nitrogen molecules, the volumes of micropores determined from experiments with nitrogen W_0^A will naturally be greater than those found from experiments with benzene W_0^B .

4. From the results of the present investigation we may infer that the adsorption properties of active carbons can with equal justification be assessed from adsorption measurements on benzene vapor at 20° or on nitrogen at -195° over a wide range of equilibrium relative pressures. However, owing to the small dimensions of the nitrogen molecule, the ultraporosity effect is very apparent for finely porous active carbons. This leads to higher values for the limiting volumes of adsorption space W_0^A , as compared with the analogous volumes W_0 that are of significance for vapors of practical interest. Hence, the constants W_0 determined from experiments with nitrogen as standard vapor cannot be used without supplementary experimental data for any exact calculations from Equation (1) of the adsorption of other vapors at different temperatures and relative pressures. When the temperature is varied, the values of saturated vapor pressure p_s at these temperatures are taken from tables.

Benzene molecules do not differ substantially in dimensions from molecules of vapors of technical interest. In particular, the possible error due to the ultraporosity effect is unlikely to differ by more than $\pm 7\%$ from the value of W_0 found from the adsorption isotherm of the standard vapor, benzene [19]. Hence, the constants W_0 and B determined from the adsorption isotherm for benzene vapor can be used in calculations of adsorption isotherms of values of the adsorption of other vapors at a given temperature T from Equation 1 to the adsorption isotherm. If it is known that $W_0^A/W_0^B = 1$ for the given type of active carbon, then its adsorption properties with respect to benzene vapor will be characterized in just the same way whether benzene vapor or nitrogen vapor is used.

5. The determination of limiting volumes of adsorption space W_0 for an active carbon with adequate accuracy from the adsorption isotherm equation for vapors of various substances having molecules of different sizes opens up the possibility of studying the size-distribution of the micropore volume by the method of "molecular probes" [6, 10]. If ΔW_0 is the difference in limiting volumes of adsorption space for two vapors with different effective molecular dimensions r_1 and r_2 , then the differential volume of micropores of mean radius $\bar{r} = \frac{1}{2}(r_1 + r_2)$ will be expressed by

$$v_d = \frac{\Delta W_0}{\Delta r}, \quad (16)$$

in which

$$\Delta r = r_2 - r_1. \quad (17)$$

With the aid of a selection of substances having molecules of different dimensions and of approximately spherical form (e.g. neopentane), it is possible to describe the distribution of most of the volume of the micropores of an active carbon. As substances with large molecules it is expedient to select fluoro-hydrocarbons, because they give considerably higher saturated vapor pressures. As the molecular weight of the substance increases it is naturally necessary to measure the adsorption isotherms at a correspondingly higher temperature. The temperature independence of W_0 follows from the potential theory of adsorption.

SUMMARY

1. The adsorption properties of several samples of active carbons with respect to benzene vapor at 20° and to nitrogen vapor at -195° were studied in detail.
2. It was shown that in both cases adsorption is due to dispersion interaction of vapor molecules with the active carbon surface. Affinity coefficients of the characteristic curves of nitrogen were calculated.
3. The main causes for the differences in the sorption volumes of nitrogen and benzene at the start of hysteresis on the adsorption isotherms were analyzed.
4. More rational methods were proposed for the determination of the volumes of micropores and intermediate pores of active carbons of the first structural type.
5. The question of the choice of a standard vapor for the characterization of the adsorption properties of active carbons was discussed.

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RADIATION-INDUCED REACTIONS OF ORGANIC SUBSTANCES
COMMUNICATION 3. TRANSFORMATIONS OF ETHYLENE
PRODUCED BY FAST ELECTRONS•

B. M. Mikhailov, V. G. Kiselev, and V. S. Bogdanov

The action of high-energy radiation on ethylene was first studied by Mund and Koch [2]; they found that under the action of α -particles ethylene is converted into hydrogen, methane, and liquid substances having the odor of kerosene or turpentine. Lind and co-workers [3] irradiated ethylene with α -particles and obtained hydrogen, a little methane and ethane, and some liquid substances, which they did not investigate. McLennan and Patrick [4] studied the radiolysis of ethylene by cathode rays, and in the reaction products they detected not only H_2 and CH_4 , but also acetylene; they showed that the liquid substances, which they did not investigate. McLennan and Patrick [4] studied the radiolysis of ethylene by cathode rays, and in the reaction products they detected not only H_2 and CH_4 , but also acetylene; they showed that the liquid substances formed were unsaturated. The action of γ -rays on ethylene has been investigated recently [5-7]. It was found that under some conditions ethylene is converted by γ -rays either into liquid products or into polyethylene, and the yields with respect to energy consumed attains several thousand molecules per 100 ev, which indicates the occurrence of chain reactions.

In the present investigation we have studied the transformations of ethylene under the action of fast electrons under various conditions. We investigated the effect of the duration of irradiation, the initial pressure, and the dilution of the ethylene with nitrogen and hydrogen. Both the liquid and gaseous reaction products were analyzed.

In experiments on the irradiation of pure ethylene for 30 minutes at an initial pressure of 1 atm the extent of decomposition was 35% on the average. In the chromatographic separation of gas mixtures obtained as a result of irradiation it was found that the gaseous reaction products consist mainly of hydrocarbons having an even number of carbon atoms and contain only traces of CH_4 . Table 1 gives the composition of the gaseous reaction products and the yields on the ethylene that reacted (yields of CH_4 , C_2H_6 , C_2H_2 , C_4H_{10} , C_4H_8 are calculated in terms of carbon).

TABLE 1
Composition of Gaseous Products of the Irradiation of Ethylene and the Yields of Products on the Ethylene that Reacted

Reaction product	CH_4	C_2H_6	C_2H_2	C_4H_{10}	C_4H_8	H_2
Content in the gas mixture (without ethylene) (%)	7	7	39	28	4	15
Yield (%)	1,2	2,4	12,7	16,3	2,9	5,0

• For Communication 2 see [1].

It will be seen from Table 1 that the main gaseous products of the radiolysis of ethylene are butane and acetylene, and not hydrogen and methane, as stated by all previous investigators [2-4].

We must point out that, in composition, the radiolysis products of ethylene obtained by the action of fast electrons are greatly different from the pyrolysis products, which include hydrocarbons containing both even and odd numbers of carbon atoms [8], and from the gaseous products of the polymerization of ethylene under the action of an electric discharge, which consist mainly of hydrogen, ethane, acetylene, and 1-butene [9]. This difference in the products of the decomposition of ethylene under various conditions gives reason to suppose that the mechanism of the transformations of ethylene produced by fast electrons is different from that of the transformations of ethylene under the action of electric discharges.

TABLE 2
Relation of Conversion and Yield of Radiolysis Products (% on ethylene that reacted, as carbon) to Exposure

Reaction product	Exposure (minutes)		
	15	30	45
CH ₄	2	1,2	1,5
C ₂ H ₆	2	2,4	2,1
C ₂ H ₂	17,5	12,7	10,6
C ₄ H ₁₀	23,1	16,3	15,6
C ₄ H ₈	0,5	2,9	2,5
H ₂	2,5	5	5,7
Conversion	16	35	42,5

In order to determine the effect of time on the course of the process we carried out experiments on the irradiation of ethylene at various exposure times with other conditions constant. The results of these experiments are given in Table 2.

Table 2 shows that with shortening of the duration of irradiation the yields of butane and acetylene rise rapidly, whereas the yields of other hydrocarbons, which are very low, change very little. This can be regarded as confirmation of the view that acetylene and butane are primary products of the radiolysis of ethylene under the action of fast electrons.

We carried out experiments also on the radiolysis of a mixture of 75% of ethylene and 25% of hydrogen at an exposure of 30 minutes. Analysis of the gaseous mixtures showed that the reaction products are the same and (with the exception of methane, which is obtained in somewhat higher yield) are obtained in the same relative amounts as in the experiments with pure ethylene. It is clear that molecular hydrogen does not hydrogenate ethylene at all under the action of fast electrons. Experiments on the irradiation of ethylene at various initial pressures showed that reduction of pressure from 1 atm to 0.25 atm has no effect on the composition of the reaction products, but increases the degree of decomposition of ethylene somewhat (Fig. 1).

Table 3 gives the results of experiments on the irradiation of ethylene diluted with various proportions of nitrogen at an exposure of 30 minutes. Comparison of the results of individual experiments given in Table 3 shows that dilution of ethylene with nitrogen, while greatly increasing the degree of decomposition of ethylene and the yield of hydrogen, greatly reduces the yield of gaseous hydrocarbons. Nitrogen, therefore, acts as an energy carrier; it also affects the character of the reaction appreciably, though this effect is difficult to explain. Fig. 1 gives a graphical representation of the relation of the degree of decomposition of ethylene to the initial pressure and the dilution with nitrogen; the pressure and concentration of ethylene are given on the same scale (the concentration of ethylene in mixtures with nitrogen is expressed as a partial pressure). It must be pointed out that both with reduction of pressure and with dilution with nitrogen the yield per 100 ev (G) falls; for pure ethylene this yield was determined in special dosimetric experiments and was found to be 16 molecules per 100 ev. The same quantity can be obtained from a formula proposed for the determination of G in the polymerization of ethylene under the action of γ -radiation [6]. This formula has the form:

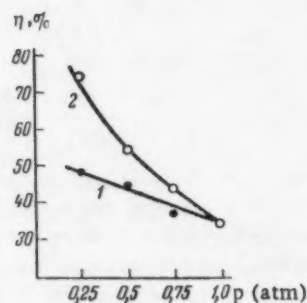


Fig. 1. Relation of degree of decomposition of ethylene (η) to the initial pressure and to the dilution with nitrogen: 1) effect of reduction of pressure; 2) effect of dilution.

$$G = 16 + 1,49 \left(\frac{A}{B} \right)^{\frac{1}{2}},$$

In which A is a quantity depending on the density of ethylene and B is a quantity depending on the ionization density. The ratio A/B is the greater, the greater the contribution of chain processes, and it becomes zero when these processes are absent. It follows that the radiolysis of ethylene under the action of fast electrons does not proceed by a chain mechanism.

TABLE 3
Relation of the Yields of Gaseous Reaction Products (% on ethylene that reacted) and the Degree of Decomposition to the Nitrogen Content of the Original Mixture

Reaction product	Nitrogen content of mixture (%)			
	0	25	50	75
C_2H_2	12,7	8,5	6,3	4,5
C_4H_6	2,9	1,5	1,0	—
C_nH_{2n+2}	12,6	8,5	7,0	6,0
H_2	5,0	6,5	9,5	9,0
Degree of decomposition (%)	35	44	55	75
Yield of gaseous products (without H_2)	28,2	18,5	14,3	10,5

In order to establish the composition of the liquid polymerization products we carried out an experiment on the irradiation of ethylene in a circulatory flow system: the gas was passed into the reaction space from a cylinder at a rate of 5.5 liters/hour and, passing through a trap cooled to -80° , was partially returned by means of a fan into the reaction space at a rate of 30-32 liters/hour, which corresponds to an exposure of 3.4 minutes. In the course of the experiment, which lasted for 71 hours, 380 liters of ethylene was passed into the system; by the end of the experiment 73.5 g of liquid products had collected, and these were fractionally distilled. For the resulting fractions we determined refractive indices, molecular weights, and contents of double bonds by the bromine-value method and by sulfonation. The results are given in Table 4.

TABLE 4

Fraction	Amount (% on total mass)	B.p. in $^\circ C$ (p in mm)	n_D^{20}	Mol. wt.	Degree of unsaturation (from bromine value)	Total content of aromatic and unsaturated hydrocarbons
I	1,2	42-63	1,3740	86,5	—	—
II	5,5	63-69	1,3815	88,0	26	12,5
III	9,1	69-130	1,4060	114,5	39	30
IV	9,0	130-190	1,4330	149	79	52
V	10,6	115-165 (20)	1,4670	225	73	58
VI	11,8	165-215 (20)	1,4830	265	57	66
VII	19,1	215-270 (20)	1,4930	305	88	71
VIII	9,7	250-290 (10)	1,5035			
Residue in still	9,9					

Comparing these data with the corresponding constants of known hydrocarbons, we may conclude that Fractions I-III consist of hexanes, hexenes, octanes, and octenes, the unsaturated hydrocarbons being predominant. The molecular weights and the fractionation curve (Fig. 2) show that these fractions do not contain appreciable amounts of C_5 and C_7 hydrocarbons.

As Table 4 shows, the radiolysis of ethylene does not lead to the formation of benzene and its nearest

homologs, whereas the higher fractions contain considerable amounts of aromatic hydrocarbons; in particular Fractions VII and VIII may contain aromatic condensed systems containing more than two rings, and inference which may be made from the fact that these fractions fluoresce strongly in ultraviolet radiation.

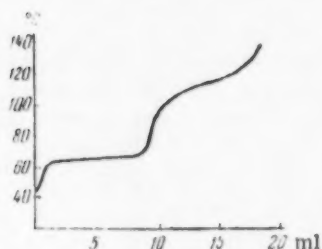
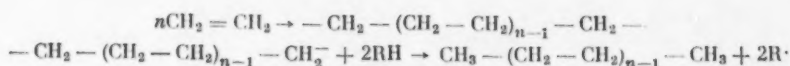


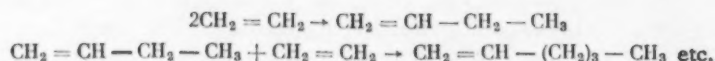
Fig. 2. Fractionation curve for a mixture of radiolysis products of ethylene.

Hence, the available material, despite its incompleteness, enables us to reach some conclusions concerning the mechanism of the radiolysis of ethylene under the action of fast electrons. The first main direction of the process consists in the formation of saturated hydrocarbons having an even number of carbon atoms, which is an indication of the polymerization of ethylene without cleavage of the carbon skeleton of the original molecules or of the polymers formed. It is probable that the polymerization of ethylene in the first stage of radiolysis consists in the formation

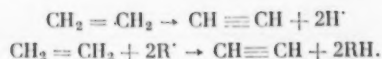
of diradicals with an even number of carbon atoms ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$ etc.) and their conversion into saturated molecules by collision with other molecules and with ethylene molecules in particular, e.g.



Such diradicals will probably be partially converted into the corresponding olefins, which will explain the presence of butenes and hexenes among the radiolysis products. The formation of olefins can occur also by the mechanism assumed for the polymerization of ethylene under the action of an electric discharge [9]:



The second main direction of the radiolysis of ethylene under the action of fast electrons consists in the dehydrogenation of ethylene to acetylene. The formation of acetylene can be explained both by direct dehydrogenation with liberation of free hydrogen and by the dehydrogenation of an ethylene molecule on collision with free radicals:



In conclusion it must be mentioned that in most experiments on the radiolysis of ethylene, traces of propene can be detected among the products; this may be explained by partial methylation of ethylene by methyl radicals formed in small quantities.

EXPERIMENTAL

The irradiation of ethylene with an electron stream was carried out in a brass chamber, capacity 2 liters, having the form of a cylinder rounded at the end carrying the outlet aperture. The electron beam passed into the chamber through aluminum foil from a linear accelerator (voltage across tube 120 kv, outgoing current 90-92 μa). The ethylene was passed into the chamber through drying vessels containing solid potassium hydroxide and phosphoric oxide. In static experiments the C_2H_4 content of the ethylene was 98.2%, and in the circulatory-flow experiment the original gas contained 93.5% of ethylene. The pressure in the chamber was measured with an open mercury monometer.

The gaseous reaction products were analyzed in a VTI-2 apparatus and with a VNIGNI No. 4 chromatograph, which enabled us to determine all the gaseous hydrocarbons separately (without separation of isomers). The liquid radiolysis products were condensed in glass traps at -80° and were fractionated up to 190° through a 35-cm column having a metal filling. The residue was vacuum-fractionated from a Claisen flask.

The content of unsaturated hydrocarbons was determined by bromination by McIlhiney's method [10]. The approximate determination of the total content of aromatic and unsaturated hydrocarbons was carried out by Kattwinkel's method [10].

SUMMARY

1. In its radiolysis ethylene is converted mainly into butane, acetylene, and liquid hydrocarbons.
2. Apart from butane and acetylene, the gaseous products include small amounts of CH_4 , C_2H_2 , C_4H_6 , and H_2 and also traces of propene. The liquid products boiling up to 130° consist of C_6 and C_8 aliphatic hydrocarbons. The higher fractions contain considerable amounts of aromatic and unsaturated hydrocarbons.
3. The formation of butane, hexanes, octanes, and other higher alkanes proceeds by the condensation of aliphatic diradicals having even numbers of carbon atoms with one another and subsequent hydrogenation.
4. The yield in the reaction is 16 molecules per 100 ev.
5. Reduction of the initial pressure raises the extent of the decomposition of ethylene without affecting the course of the reaction. Dilution of the ethylene with nitrogen considerably increases the degree of conversion with a sharp lowering of the yield of gaseous hydrocarbons. Dilution with hydrogen has almost no effect on the radiolysis of ethylene.

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PHYSICAL AND CHEMICAL PROPERTIES OF WS_2 CATALYSTS

COMMUNICATION 2. ADSORPTION PROPERTIES OF MIXED WS_2 - CLAY CATALYSTS

S. M. Samoilov and A. M. Rubinshtein

A catalyst consisting of WS_2 (8-10%) and clay and activated with HF is used in presence of hydrogen under pressure for the preferential cleavage and isomerization of hydrocarbons with only slight hydrogenation. The conditions for the hydrogenation of individual hydrocarbons and their mixtures and for the industrial "gasolinization" of medium oils, and also the compositions and properties of the resulting products, are described in detail in various patents and papers, e.g. [1-7]. In this catalyst clay acts simultaneously as a carrier and as an active component which increases the cleaving and isomerizing power and reduces the hydrogenating power as compared with an unmixed WS_2 catalyst [1,3].

In spite of the great practical importance of catalysts consisting of WS_2 and clay, we have not found a single paper concerned with the adsorption properties of such catalysts and their comparison with those of the clays used. For an unmixed WS_2 catalyst it has been shown [8] that, depending on the conditions of thermal treatment, its specific surface calculated from the BET equation varies from 3 to 66 sq.m/g and its catalytic activity varies symbatically with the change in specific surface and pore volume.

In the present investigation we studied the adsorption properties of two catalysts consisting of WS_2 and clays (terrana and Tavtman clays) and used previously for the hydrogenolysis of individual hydrocarbons and medium oils under laboratory and works conditions [2, 4, 6, 7, 9, 10]. We investigated also the adsorption properties of the clays forming components of these catalysts. The adsorption properties were studied and compared by measuring the adsorption of nitrogen vapor at the temperature of liquid nitrogen and the adsorption of toluene from its solution in isooctane at room temperature.

EXPERIMENTAL

For the investigation we used the clays terrana (I) and Tavtman clay (II) and the catalysts 8% WS_2 -terrana (No.1) and 8% WS_2 -Tavtman clay (No. 2) prepared in identical fashion by impregnation of the clay with ammonium thiotungstate solution and subsequent thermal decomposition. The conditions of preparation are described in greater detail in [9, 10].

The adsorption of nitrogen vapor by the catalysts at the temperature of liquid nitrogen was measured by the gravimetric method, as described in [8] with the same activation of the samples at 400° before measurement of the isotherms. It was shown that the results were reproducible 1) by repeated measurements of adsorption and desorption isotherms on each sample (before some of the measurements the adsorbent was degassed in high vacuum at 400° to constant weight) and 2) by determining the isotherms on two different samples of Catalyst No. 1. The adsorption isotherms of nitrogen vapor at the temperature of liquid nitrogen are shown in Figures 1 and 2.

The pore volume was calculated from the saturation point and the specific surface from the BET equation (Figures 3 and 4), for which purpose the molecular area ω_0 for N_2 was taken to be 16.2 Å². The radius-distribution of pore volume was calculated from the adsorption isotherms by the Kelvin equation without consideration of the thickness of the adsorption film (Fig. 5). It was assumed conditionally that this equation holds for pores of

effective radius greater than 10 Å. As no capillary-condensation hysteresis was detected for Catalyst No. 2, calculation for this catalyst by the Kelvin equation is provisory.

The adsorption of toluene from its solution in isooctane was measured by the method described in [11]. We used twenty solutions of various concentrations prepared from toluene (n_D^{20} 1.4958) and standard isooctane (n_D^{20} 1.3912). The ground adsorbent was placed in a well-stoppered glass tube. The solution was poured simultaneously into the tube containing adsorbent and into a control tube, and the tubes were then kept at room temperature for one day. As special experiments showed, this time is considerably greater than that necessary for the attainment of adsorption equilibrium. When the adsorption was complete, the refractive indices of the solutions from the tube containing adsorbent and from the control tube were measured with an IRF-23 refractometer (Pulfrich type).

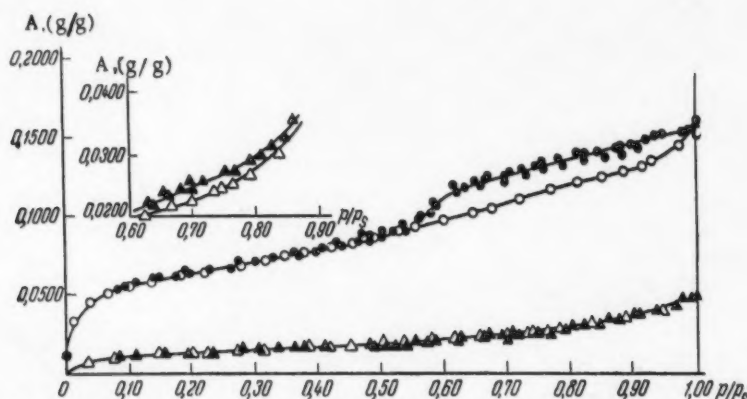


Fig. 1. Adsorption isotherms for nitrogen vapor at the boiling point of liquid nitrogen on clays forming components of mixed WS_2 catalysts: o - Clay I; Δ - Clay II (black points represent desorption).

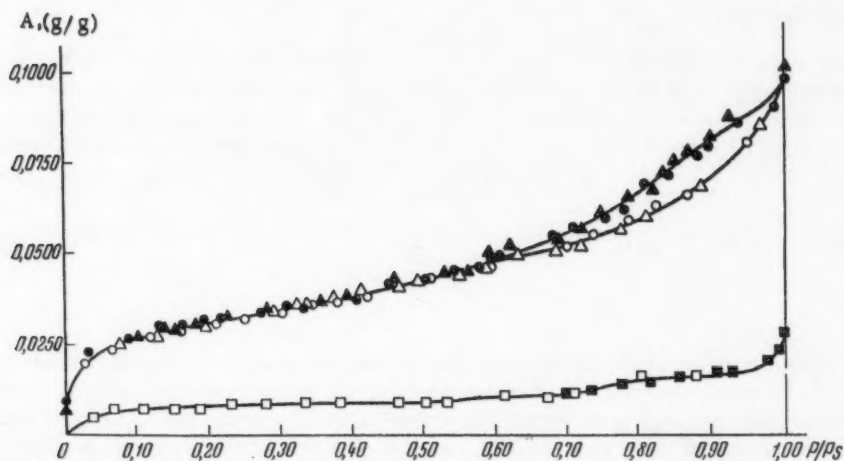


Fig. 2. Adsorption isotherms for nitrogen vapor at the boiling point of liquid nitrogen on mixed WS_2 catalysts: o - Catalyst No. 1; Δ - parallel experiment on another sample; \square - Catalyst No. 2 (black points represent desorption).

After the first experiment on the adsorption of toluene from its solution in isooctane the adsorbent was dried in a vacuum drying oven at a residual pressure of 5-10 mm for one hour at 250° and was evacuated under these

conditions for four hours. When the adsorbent had cooled to room temperature the experiment on the adsorption of toluene from its solution in isooctane was repeated. It was found that for Catalyst No. 1 and Clay II in the first and subsequent experiments the same change in refractive index occurred if the original solutions were identical. In the case of Catalyst No. 2 impurities were washed out in the first experiment, and in the second and subsequent experiments identical changes in refractive index occurred: the results of the first determination were therefore rejected. The adsorption isotherms for toluene from a solution in isooctane at room temperature are shown in Figures 6 and 7. Owing to the small amount of Clay I at our disposal we made no measurements on the adsorption of toluene from its solution in isooctane on this clay.

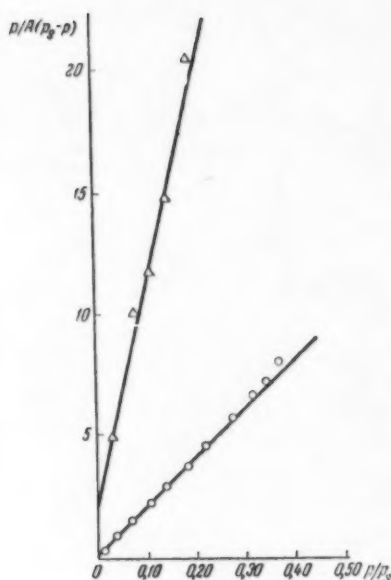


Fig. 3. Application of the BET equation to adsorption isotherms for nitrogen vapor on clays forming components of mixed WS_2 catalysts (see Fig. 1): \circ - Clay I; \square - Clay II.

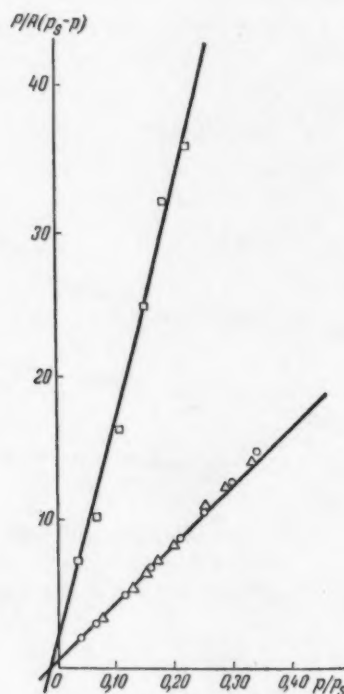


Fig. 4. Application of the BET equation to adsorption isotherms for nitrogen vapor on mixed WS_2 catalysts (see Fig. 2): \circ - Catalyst No. 1; Δ - parallel experiment with another sample; \square - Catalyst No. 2.

The adsorption space V_a and its content of toluene \underline{a} were calculated from Kiselev's equation [12]:

$$\underline{a} = x + V_a \cdot c; \quad V_a = - \left(\frac{\partial x}{\partial c} \right)_a,$$

in which \underline{x} is the amount of adsorbed toluene and \underline{c} is the equilibrium concentration of toluene. In the investigation [11] it was shown that for solutions of toluene in isooctane the refractive index \underline{n} is a linear function of the toluene concentration expressed in moles per liter and of the density of the solution (Fig. 8, constructed from data in [11]). Hence, for the determination of V_a we plot the refractive index of the equilibrium solution (n_e) as abscissa and the quantity

$$x = \frac{V(n - n_e)}{m},$$

as ordinate (m is the amount of adsorbent, and V is the volume of solution, which is determined without taking account of contraction from the weight of solution and its density as found from refractometric data).

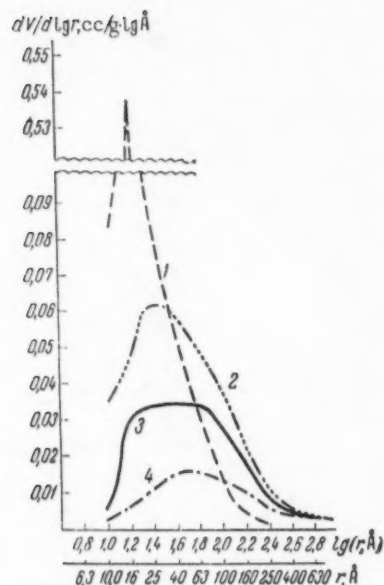


Fig. 5. Distribution of pore volume with respect to effective radius for the investigated mixed WS_2 catalysts and clays calculated from the nitrogen adsorption isotherms given in Figures 1 and 2: 1) Clay I; 2) Catalyst No. 1; 3) Clay II; 4) Catalyst No. 2.

DISCUSSION OF EXPERIMENTAL RESULTS

As will be seen from the table and Figures 1, 3, and 5, Clays I and II have different structures. The results on the adsorption of nitrogen vapor at the temperature of liquid nitrogen show that the pore volume of Clay I is 3 times as high as that of Clay II, while its specific surface is 5 times as great. Clay I has pores of effective radius 10-150 Å; pores of radius about 15 Å greatly predominate, and there are some pores of radius less than 10 Å. The predominating pores in Clay II are larger than in Clay I, being of radius 15-250 Å.

The table and Figures 2, 4 and 5 show that in the preparation of the catalysts the pore volume and the specific surface of the clay carrier are reduced by about one-half, both for Clay I and for Clay II. As a result, the pore volume and specific surface of Catalyst No. 1, as calculated from the adsorption of nitrogen vapor at the temperature of liquid nitrogen, are about four times as great as these quantities for Catalyst No. 2. Hence, although in the preparation of the catalysts investigated there is a reduction in the pore volume and specific surface of the clay carrier, the pore volume and specific surface of the mixed catalyst are the greater, the greater the values of these quantities for the clay component of the catalyst. Both catalysts are nonuniformly porous adsorbents having pores of effective radius 10-250 Å and greater, but in Catalyst No. 1 the predominant pore radius is less than in Catalyst No. 2. As will be seen from Fig. 5, the volume of pores of effective radius less than 10 Å in Catalyst No. 1 is considerably greater than in Catalyst No. 2.

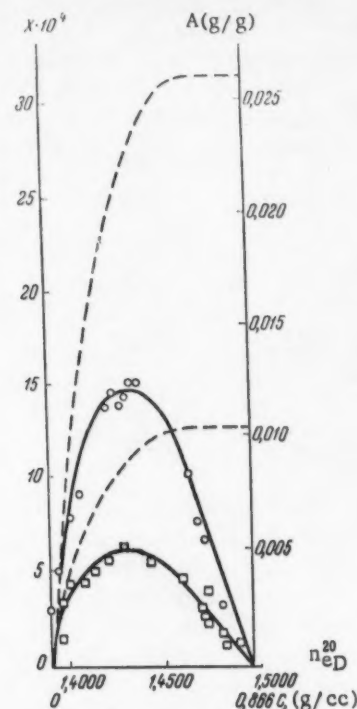


Fig. 6. Isotherms of the adsorption of toluene from its solution in isooctane at room temperature on mixed WS_2 catalysts: \circ - Catalyst No. 1; \square - Catalyst No. 2 (x is expressed in cc. (refractive index) / g; c and n_D are concentration of toluene and refractive index of the equilibrium solution); the broken line shows the total toluene content of the adsorption space.

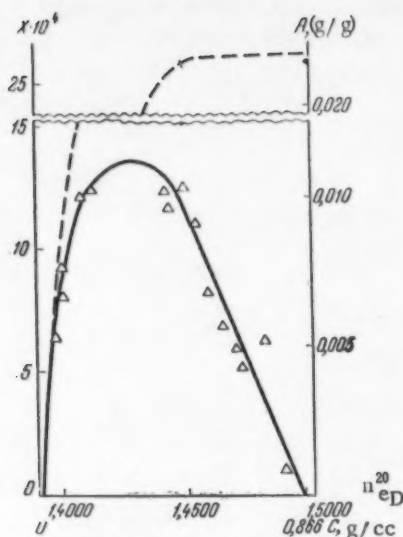


Fig. 7. Isotherm of the adsorption of toluene from its solution in isooctane at room temperature on Clay II. The broken line shows the total toluene content of the adsorption space.

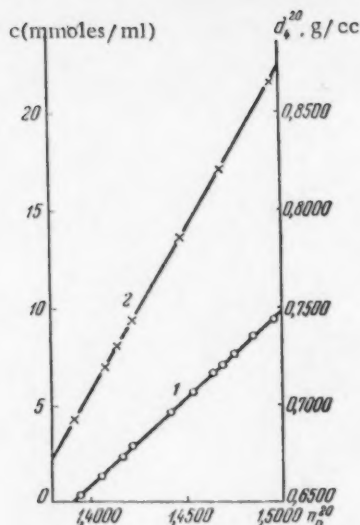


Fig. 8. Relation of the refractive index of an isooctane solution of toluene to 1) the toluene concentration in the solution and 2) its density at room temperature (from data in [11]).

TABLE

Some Adsorption Characteristics of WS_2 -Clay Catalysts and Clay Carriers Determined by the Adsorption of Nitrogen Vapor at the Temperature of Liquid Nitrogen and by the Adsorption of Toluene from Solution in Isooctane at Room Temperature

Adsorbent	According to adsorption of nitrogen			According to adsorption of toluene	
	specific surface (sq. m/g)	no. of molecules in monolayer (per g)	pore volume (cc/g)	adsorption volume (cc/g)	no. of molecules in adsorption volume (per g)
Clay I (Terrana)	183		0.1966		
Clay II (Tavtiman clay)	36	$2.2 \cdot 10^{20}$	0.0635	0.025	$1.4 \cdot 10^{20}$
WS_2 -terrana (No. 1)	87	$5.4 \cdot 10^{20}$	0.1278	0.030	$1.7 \cdot 10^{20}$
WS_2 -Tavtiman clay (No. 2)	21	$1.3 \cdot 10^{20}$	0.0344	0.012	$0.7 \cdot 10^{20}$

The results of experiments on the adsorption of toluene from its solution in isooctane, given in the Table and in Figures 6 and 7, are in close accord with the conclusions based on the results on the adsorption of nitrogen vapor at the temperature of liquid nitrogen. Actually, the adsorption volume of Catalyst No. 1 as determined by the adsorption of toluene is 2.5 times as great as that of Catalyst No. 2. A more detailed examination of the results on the adsorption of nitrogen and toluene shows that the number of toluene molecules filling the adsorption volume at its saturation is less for all investigated adsorbents than the number of nitrogen molecules covering these adsorbents as a monolayer (see Table). The molecules of toluene, being larger than those of nitrogen, do not penetrate into the fine pores of the adsorbents. Analogous phenomena were noted in the investigations [13, 14] and also in [11]. It is interesting that the greatest difference in the numbers of nitrogen and toluene molecules is found for Catalyst No. 1, in which the fine pores occupy a considerable volume.

The catalytic activities of the catalysts described can be estimated from the degrees of conversion in the hydrogenation of benzene and cyclohexane as obtained in the investigation [4], which was carried out with these same samples of catalysts (420° , initial hydrogen pressure 140 atm). When hydrogenated in this way benzene was

converted into cyclohexane, methylcyclopentane, and cleavage products to the extent of 42% over Catalyst No. 1 and 33% over Catalyst No. 2 under identical conditions; cyclohexane was converted into methylcyclopentane and cleavage products to the extent of 71% over Catalyst No. 1 and 21% over Catalyst No. 2. Hence, reduction in the activity of the investigated catalysts in the hydrogenation, isomerization, and cleavage reactions of benzene and cyclohexane proceeds parallel with reduction in specific surface and pore volume.

SUMMARY

1. The adsorption characteristics of two mixed WS_2 catalysts and of clays forming components of these catalysts (terrana and Tavtman clay) were determined from adsorption measurements on nitrogen vapor at the temperature of liquid nitrogen and toluene from its solution in isooctane at room temperature.

2. Investigation of the specific surfaces and porous structures of the mixed WS_2 catalysts and their component clays showed that these properties of the catalyst are mainly determined by the same properties of the clay carrier. With the given method of preparation, the specific surfaces and pore volumes of the mixed catalysts are less than for the component clays.

3. It was shown by experiments on the adsorption of toluene from its solution in isooctane that the number of toluene molecules in the adsorption volume of a WS_2 catalyst is less than the number of nitrogen molecules in a monolayer in the adsorption of nitrogen at the temperature of liquid nitrogen.

4. From a consideration of the data in [4] in relation to the adsorption properties of the same samples of catalysts, as reported in the present paper, it follows that there is a symbatic relationship between catalytic activity for the transformations of benzene or cyclohexane at 420° at an initial hydrogen pressure of 140 atm and the specific surface and pore volume.

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PHYSICAL AND CHEMICAL PROPERTIES OF WS_2 CATALYSTS
COMMUNICATION 3. PHASE COMPOSITION AND ADSORPTION
PROPERTIES OF THE MIXED CATALYST $WS_2 - NiS - Al_2O_3$

S. M. Samoilov and A. M. Rubinshtein

A catalyst consisting of 25% of WS_2 , 5% of NiS , and 70% of Al_2O_3 (all by weight) is widely used for the laboratory and industrial hydrogenation of various individual hydrocarbons and their mixtures [1-12]. As compared with an unmixed WS_2 catalyst, it has a higher activity in the hydrogenation of unsaturated bonds of all types and a considerably higher activity in the reduction and hydrogenation of phenols. On the other hand its activity in isomerization and cleavage reactions is appreciably less than that of an unmixed WS_2 catalyst [2, 3, 6-10].

In spite of the valuable properties of the mixed catalyst $WS_2 - NiS - Al_2O_3$, its structure has not been studied in detail: only one investigation [9] has been reported, and in this the phase composition was examined with the electron microscope. At a magnification of 14,000 it was possible to see small aggregates of WS_2 crystals distributed fairly sparsely in a highly dispersed porous mass of $\gamma-Al_2O_3$. The authors did not observe NiS crystals. In the investigation [9] a similar study was made of an unmixed WS_2 catalyst, in which large conglomerates of crystals of considerable density were observed. The authors concluded that the enhanced activity of the catalyst $WS_2 - NiS - Al_2O_3$ in hydrogenation reactions is due to the increased working surface of WS_2 and the easier access to reagents, as compared with an unmixed WS_2 catalyst. The authors consider that, owing to the lower content of WS_2 in the catalyst $WS_2 - NiS - Al_2O_3$, "each crystal or aggregate of crystals has to do more work than in the case of pure WS_2 ", and on this basis they explain the more rapid loss of activity in the $WS_2 - NiS - Al_2O_3$ catalyst than in the unmixed WS_2 catalyst.

In the investigation [3], in which a study was made of the dependence of the catalytic activity of WS_2 catalysts on the dimensions of the tablets of catalyst in the hydrogenation and cleavage of mixtures of hydrocarbons, it was noted that the large reactant molecules penetrate much more readily into the pores of the $WS_2 - NiS - Al_2O_3$ catalyst than into those of the unmixed WS_2 catalyst.

In considering the point of view taken in [9] we must point out in the first place that it is based not on direct measurements of specific surface and pore radius and not on a quantitative statistical appraisal of electron microscope data, but only on a purely qualitative description of the different regions distinguished on the catalyst surface. Moreover, it is known that heterogeneous catalysis is a surface phenomenon; hence, the explanation of the more rapid deactivation of the mixed as compared with the unmixed WS_2 catalyst by the greater load imposed on the crystal, i.e. on the bulk system and not on unit area of its surface, does not give a correct concept of the relation between the properties of these catalysts.

Another explanation of the part played by Al_2O_3 in determining the difference in activity and selectivity between $WS_2 - NiS - Al_2O_3$ and pure WS_2 was suggested by Pier [7], who considers that Al_2O_3 is not simply a carrier affecting the porous structure of the catalyst, but an active component participating in the determination of the specific properties of the catalyst $WS_2 - NiS - Al_2O_3$. Pier considers that Al_2O_3 cannot be replaced by another component having an equally strongly developed surface*.

* This finds confirmation, for example, in the fact that, in spite of the large surface of the mixed catalyst $WS_2 - NiS - Al_2O_3$, this catalyst has a lower hydrogenating and higher cleaving power than an unmixed WS_2 catalyst [13, 14].

No explanation has been given for the role of NiS, which, both in the pure state [9] and when supported on Al_2O_3 [7], has considerably less hydrogenating activity than the corresponding WS_2 catalyst. Nevertheless, small additions of NiS result in considerable increase in the hydrogenating power of a WS_2 catalyst, pure or supported on Al_2O_3 [7]. It was here noted that, in contrast to an unmixed WS_2 catalyst, with rise in hydrogenation temperature above 425° the cleavage activity of a WS_2 -NiS catalyst falls sharply and becomes equal to the cleavage activity of WS_2 -NiS- Al_2O_3 . It was shown by electronographic examination that the NiS phase is absent in the surface layers of a fresh WS_2 -NiS catalyst and appears in these layers when the catalyst has been in work for a long time, but x-ray examination revealed no difference between fresh and spent WS_2 -NiS catalyst. Pier considers that the cleavage activity of the WS_2 -NiS catalyst falls as a result of breakdown of the mixed phase in the surface layer of the catalyst.

It must be pointed out that in [7] no x-ray investigation was made of the WS_2 -NiS- Al_2O_3 catalyst and the phase composition of the mixed WS_2 -NiS catalyst is not indicated. It is known, however, that NiS exists in three allotropic modifications: amorphous α -NiS, hexagonal β -NiS with lattice parameters $a = 3.42$ Å, $c = 5.30$ Å, and $c/a = 1.55$, and the most stable form at low temperatures γ -NiS, which forms rhombohedral crystals for which $a = 9.61$ Å, $c = 3.15$ Å, and $c/a = 0.32$. The crystalline forms of NiS are associated with the phase transition β -NiS \rightarrow γ -NiS, which goes spontaneously at low temperatures. In a reducing atmosphere NiS readily passes into the subsulfide Ni_3S_2 , which has a rhombohedral lattice that differs very little from a cubic lattice: $a = 4.04$ Å and $\alpha = 90.3^\circ$ [15-18]. Different allotropic modifications are known also for Al_2O_3 . There are indications that the x-ray diagrams of crystalline WS_3 differ from those of WS_2 [19], and the form in which tungsten sulfide exists in various WS_2 catalysts is not yet clear.

For a more detailed characterization of the properties of the WS_2 -NiS- Al_2O_3 catalyst and the nature of its catalytic activity, great interest is presented by its phase composition, its specific surface, the volumes of pores accessible for molecules of various sizes, and also the distribution of pore volume with respect to radius*. In order to obtain such a detailed characterization we investigated two samples of the mixed catalyst WS_2 -NiS- Al_2O_3 by x-ray analysis, by the adsorption of nitrogen vapor at the boiling point of liquid nitrogen, and by the adsorption of toluene and benzene from their solutions in isooctane at room temperature. The activities of the catalysts investigated were determined for the hydrogenation of phenol at 380° under an initial pressure of hydrogen of 110-120 atm.

EXPERIMENTAL

Two samples of the mixed catalyst WS_2 -NiS- Al_2O_3 (No. 1 and 2) were investigated; they were prepared in identical fashion by the impregnation of different portions of Al_2O_3 in $(\text{NH}_4)_2\text{WO}_4$ and NiSO_4 solutions and subsequent decomposition of these salts in a stream of a mixture of H_2S and H_2 . The method of preparing the catalysts was described in greater detail in [4, 5]. Both samples were investigated before being used in the hydrogenation process.

The x-ray phase analysis was carried out in standard powder cameras (diameter 57.3 mm). In photography by the symmetrical method with $\text{CuK}\alpha$ radiation (Ni filter) at 35 kv and 14 ma the exposure was 8 hours (diameter of sample 0.6 mm). The determinations were repeated by the Straumanis method with Co radiation without filter at 30 kv and 14 ma with an exposure of 10 hours (diameter of sample 0.4 mm). Table 1 gives the calculated interplanar distances d and the intensities of the corresponding reflections of the two samples. For the determination of the phase composition, they were compared with the interplanar distances and reflection intensities for the relevant substances: γ - Al_2O_3 [21], nickel sulfides β - and γ -NiS [15-17], and nickel subsulfide Ni_3S_2 [18]. For WS_2 we used the results of an x-ray investigation of a compound of composition $\text{WS}_{2.05}$ with a well marked crystal structure; these results will be published in the near future.

As Table 1 shows, the γ - Al_2O_3 phase and, particularly, the WS_2 phase are readily detected by x-ray analysis. Apart from the lines due to these phases there are lines corresponding to $d = 1.678$ Å for Sample No. 1 and to $d = 1.684$ Å for Sample No. 2, which belong neither to γ - Al_2O_3 nor to WS_2 . It is evident that this is a line arising from some sulfide of nickel; in the samples investigated its intensity was low, which is in accord

* The relationship between porous structure and activity was discussed for WS_2 -NiS- Al_2O_3 catalysts in a recently published paper [20].

with the low concentration of nickel sulfide in the $WS_2-NiS-Al_2O_3$ catalyst. It should be noted that other fairly intense lines of nickel sulfide coincide with various reflections from WS_2 or $\gamma-Al_2O_3$.

TABLE 1

Phase Composition of the Mixed Catalyst $WS_2-NiS-Al_2O_3$ as Indicated by x-Ray Measurements

Cu-radiation				Co-radiation		Phase
Sample No. 1		Sample No. 2		Sample No. 1		
d	Intensity	d	Intensity	d	Intensity	
6,21	S	5,97	S *			WS ₂
4,30—4,40	S	4,32—4,43	S			Broad diffuse ring
						γ-Al ₂ O ₃ (?)
2,664	S	2,637	S	2,676	M	WS ₂
2,285	M	2,251	M	2,259	W	WS ₂ ; γ-Al ₂ O ₃
1,969	S	1,969	M	1,957	W	γ-Al ₂ O ₃
1,838	W	1,838	W	1,833	VW	WS ₂ (Ni ₃ S ₂ ; γ-NiS)
1,678	VW	1,684	W			Ni ₃ S ₂ (?)
1,588	S	1,575	S	1,570	M	WS ₂ ; γ-Al ₂ O ₃ ; (γ-NiS)
1,540	M	1,534	S	1,521	M	WS ₂ ; γ-Al ₂ O ₃ ; (γ-NiS)
1,390	S	1,392	S	1,394	M	γ-Al ₂ O ₃ ; WS ₂
		1,294	W			WS ₂ ; γ-Al ₂ O ₃ ; (Ni ₃ S ₂ ; γ-NiS)
1,244	VW					WS ₂ ; γ-Al ₂ O ₃ (Ni ₃ S ₂)
1,058	VW	1,088	W			WS ₂ (γ-NiS)
1,028	M	1,031	M	1,025	M	WS ₂
1,004	M	1,001	M	0,996	M	WS ₂

* Abbreviations: S, strong; M, medium; W, weak; VW, very weak.

TABLE 2

Some Adsorption Characteristics of the Mixed $WS_2-NiS-Al_2O_3$ Catalyst as Determined by the Adsorption of Nitrogen Vapor at the Boiling Point of Liquid Nitrogen and of Toluene and Benzene from their Solutions in Isooctane at Room Temperature

Sample No.	Determination by N_2 adsorption			Determination by toluene adsorption			Determination by benzene adsorption		
	specific surface from BET eq. (sq. m/g)	no. of molecules in a monolayer (per g)	pore vol. (cc/g)	adsorp. vol. (cc/g)	no. of molecules in ads. vol. (per g)	spec. surf. (sq. m/g) $\omega_0 34.4$ (or 50) A^2	ads. vol. (cc/g)	no. of molecules in ads. vol. (per g)	spec. surf. (sq. m/g) $\omega_0 32.3$ (or 40) A^2
1	139	$8.59 \cdot 10^{20}$	0.2049	0.040	$2.27 \cdot 10^{20}$	78 (114)			
2	99	$6.11 \cdot 10^{20}$	0.1757	0.037	$2.10 \cdot 10^{20}$	72 (105)	0.043	$2.92 \cdot 10^{20}$	94 (117)

The measurements on the adsorption of nitrogen vapor at the temperature of liquid nitrogen were carried out as described in [13] after the same vacuum treatment of the catalyst at 400° . In order to show that the results were reproducible, two portions of Sample No. 2 were investigated (Fig. 1) and several measurements of adsorption and desorption isotherms were carried out on each of them; after several determinations had been carried out on one sample, it was degassed at 400° in a high vacuum. The adsorption isotherms for nitrogen vapor at the temperature of liquid nitrogen on Samples No. 1 and 2 are shown in Fig. 1. The calculation of the specific surfaces of the catalysts and the distribution of their pore volume with respect to effective radius was carried out as described in [13, 14] (Figures 2 and 3; Table 2).

Measurements of the adsorption of toluene and benzene from their solutions in isooctane at room temperature and calculation of the adsorption space occupied by toluene and benzene were carried out as in [14]; for the adsorption measurements on benzene we took five solutions of various concentrations in the preparation of which benzene of $n_D^{20} 1.5012$ was used. The reproducibility of the results on the adsorption of toluene was confirmed by the fact that for each sample the change in refractive index was the same in the first and every

succeeding experiment when identical original solutions were used. Only one experiment was carried out on the adsorption of benzene on a fresh Sample No. 2, so that the reproducibility of these results was not proved. For the calculation of the adsorption volume of benzene it was assumed, on analogy with the isooctane solution of toluene, that the refractive index of an isooctane solution of benzene is a linear function of the benzene concentration and of the density of the solution. The isotherms for the adsorption of toluene and benzene from their solutions in isooctane on Samples No. 1 and 2 are shown in Figures 4 and 5.

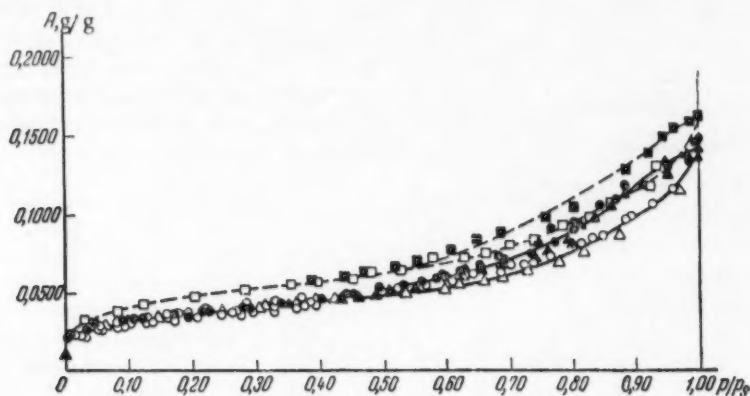


Fig. 1. Adsorption isotherms for nitrogen vapor at the boiling point of liquid nitrogen on $WS_2 - NiS - Al_2O_3$ catalysts: \square - Sample No. 1; \circ - Sample No. 2; Δ - parallel experiment with another portion; the black points refer to desorption.

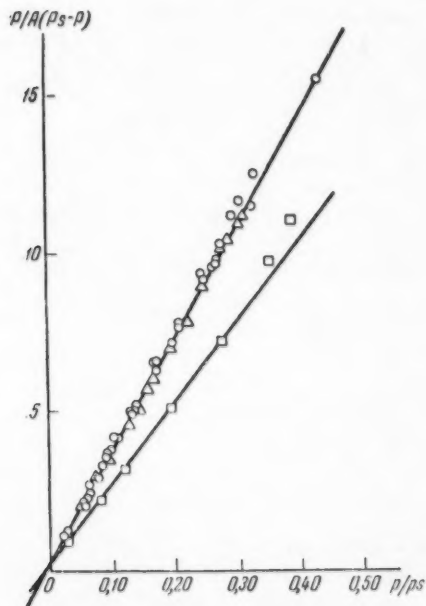


Fig. 2. Application of the BET equation to the isotherms of the adsorption of nitrogen vapor on $WS_2 - NiS - Al_2O_3$ catalysts (see Fig. 1): \square - Sample No. 1; \circ - Sample No. 2; Δ - parallel experiment with another portion.

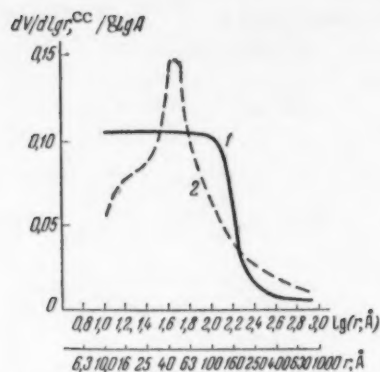


Fig. 3. Distribution of the pore volume of the $WS_2 - NiS - Al_2O_3$ catalysts investigated with respect to effective radius, calculated from the nitrogen adsorption isotherms in Fig. 1: 1) Sample No. 1; 2) Sample No. 2.

As regards nickel sulfide, the presence of this as an independent phase is indicated by the lines $\bar{d} = 1.678$ Å (Sample No. 1) and $\bar{d} = 1.684$ Å (Sample No. 2). However, the fact that the concentration of this component in the catalyst is low and many reflections of the sulfides coincide with the reflections of other components of the catalyst does not enable us to determine with certainty whether the catalyst contains γ -NiS (millerite) or the subsulfide Ni_3S_2 . As the line $\bar{d} = 1.678-1.684$ Å is almost coincident with the strong Ni_3S_2 line $\bar{d} = 1.662$ Å, it is more probable that nickel sulfide is present as the phase Ni_3S_2 , which is in keeping with the preparation of the catalyst under reducing conditions. A visual comparison of the x-ray photographs of fresh $WS_2 - NiS - Al_2O_3$ catalyst with those of active finely crystalline and inactive coarsely crystalline unmixed WS_2 catalysts shows that the WS_2 crystals in the $WS_2 - NiS - Al_2O_3$ catalyst are close in size to those in a finely crystalline WS_2 catalyst.

TABLE 3
Results on the Hydrogenation of Phenol Over $WS_2 - NiS - Al_2O_3$ Catalysts in a Rotating Autoclave at 380° for 1 Hour.
(Amount of original phenol 40 g; amount of catalyst 1 g)

Experiment No.	Sample No.	Pressure in autoclave (atm)			Amount of unchanged phenol (g)	Degree of conversion of phenol (%)
		Initial	Maximum	After cooling		
16	1	120	220	60	5.2	87
17	2	118	240	59	4.3	89
18	1	110	210	48	4.1	90

By electronographic examination • of the surface layers of individual particles of the two samples of $WS_2 - NiS - Al_2O_3$ catalyst we succeeded in detecting only the WS_2 and γ - Al_2O_3 phases. Our results on the phase analysis of the $WS_2 - NiS - Al_2O_3$ catalyst do not, unfortunately, enable us to explain the part played by nickel sulfide in this catalyst, but they indicate that in the solution of this question we must take account of the properties of Ni_3S_2 , and not only of those of NiS, as has been done in previous investigations.

• These measurements were made by V. A. Afanas'ev, to whom we express our thanks.

The hydrogenation of phenol was carried out in a 500-ml rotating autoclave. In all experiments 40 g of phenol and 1 g of catalyst were taken. The autoclave was heated for one hour, during which the temperature rose to 380° ; it was maintained at $380 \pm 10^\circ$ for one hour, and was then cooled. According to [22] and our preliminary experiments, in absence of catalyst phenol is not hydrogenated under the above conditions. The reaction products were washed several times with 10% NaOH solution, and the amount of unchanged phenol in the resulting solution was determined by titration with bromide-bromate solution [8, 23]. The results on the hydrogenation of phenol over Samples No. 1 and 2 are given in Table 3.

DISCUSSION OF EXPERIMENTAL RESULTS

As will be seen from Table 1 there can be no doubt that γ - Al_2O_3 and WS_2 are present in the fresh mixed catalyst $WS_2 - NiS - Al_2O_3$ in the form of separated crystalline phases; moreover, their lattice constants are the same as those of the pure substances.

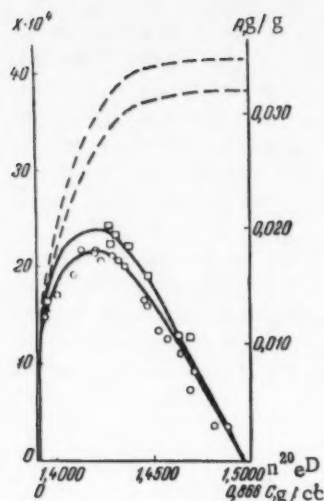


Fig. 4. Isotherms of the adsorption of toluene from its solution in isooctane at room temperature on WS_2 - NiS - Al_2O_3 catalysts: \square - Sample No. 1; \circ - Sample No. 2 (x is expressed in cc. (refractive index) / g; c and n_e are toluene concentration and refractive index of the equilibrium solution); the broken line shows the total toluene content of the adsorption space.

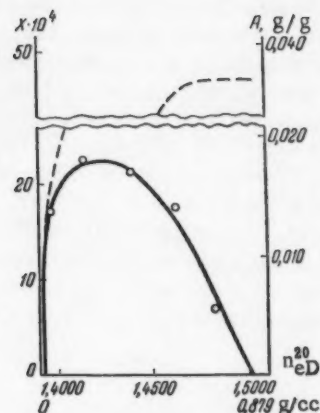


Fig. 5. Isotherm of the adsorption of benzene from its solution in isooctane at room temperature on a WS_2 - NiS - Al_2O_3 catalyst (Sample No. 2) (c is the benzene concentration in the equilibrium solution). The broken line shows the total benzene content of the adsorption space.

Passing from a discussion of the results of the adsorption measurements, we may point out that, as will be seen from Table 2 and Figures 1-3, Samples No. 1 and 2 are non-uniformly porous adsorbents whose pores vary in effective radius from less than 10 Å to more than 150 Å. In the system of coordinates that we have used there is no maximum on the curve for the distribution of the pore volume of Sample No. 1 with respect to effective radius, whereas in the case of Sample No. 2 there is a predominance of pores having an effective radius of about 50 Å. As shown in [24], the position of the maximum on the curve for the distribution of pore volume with respect to effective radius depends on the choice of coordinates.

The pore volume and specific surface of Sample No. 1 determined by the adsorption of nitrogen are greater than those of Sample No. 2. Comparison of the specific surfaces and pore volumes determined by the adsorption of nitrogen for the investigated samples of WS_2 - NiS - Al_2O_3 and an unmixed WS_2 catalyst heated in a vacuum at 400° [13] (i.e. at the temperature of the hydrogenation of hydrocarbons and phenols) shows that the specific surfaces of the WS_2 - NiS - Al_2O_3 catalysts are 1.5-2.0 times as great and their pore volumes are 3 times as great as those of the WS_2 catalyst. Also, the effective radius of the predominating pores of the comparable unmixed WS_2 catalyst is smaller (15-20 Å).

The activity of a WS_2 - NiS - Al_2O_3 catalyst depends on the distribution of its pores with respect to radius. Table 3 shows that the catalytic activities of the investigated samples for the hydrogenation of phenol under the above-indicated conditions are identical, though according to measurements of nitrogen adsorption Sample No. 1 has a specific surface that is 1.4 times as great as that of Sample No. 2. This result can be understood if we take account of the fact that there is a greater volume of fine pores having an effective radius of about 10 Å in Sample No. 1 than in Sample No. 2, so that the part of the surface that is inaccessible to phenol molecules in the hydrogenation process is greater in Sample No. 1 than in Sample No. 2. This explanation is in good accord with the results on the adsorption of toluene, the molecules of which are close in size to phenol molecules. Fig. 4 and Table 2 show that the volume of toluene absorbed at room temperature from its solution in isooctane on

Sample No. 2 is less than that adsorbed on Sample No. 1 by a factor of only 1.1.

If we compare the number of nitrogen molecules covering 1 g of a $WS_2 - NiS - Al_2O_3$ as a monolayer with the numbers of molecules of toluene and benzene in the adsorption volume of 1 g of catalyst (Table 2), it can be seen that for both samples with reduction in the size of the molecule in the series toluene, benzene, nitrogen, this number increases. Also, the adsorption volume of benzene is greater than that of toluene. It is of interest to calculate the specific surfaces accessible to toluene and benzene molecules in their adsorption from their isooctane solutions at room temperature on the assumption that they are adsorbed unimolecularly from solution [25]. The literature gives the following values of molecular area: toluene 34.4 \AA^2 [26], 50 \AA^2 [27], benzene 32.3 \AA^2 [28], 40 \AA^2 [29]. The corresponding values of specific surface are given in Table 2. Leaving aside the question of which values of molecular area are the more accurate, we see that the surface of Sample No. 2 accessible to benzene and toluene molecules is close in value to that accessible to nitrogen molecules; the surface of Sample No. 1 accessible to toluene is less than that accessible to nitrogen molecules. The surface of Sample No. 1 accessible to toluene is scarcely any greater than the corresponding value of the surface of Sample No. 2. Hence, these results confirm the above explanation of the equivalence of the two samples in catalytic activity for the hydrogenation of phenol.

SUMMARY

1. The phase composition of a $WS_2 - NiS - Al_2O_3$ hydrogenation catalyst was investigated with the aid of x-rays. It was shown that the phases WS_2 and $\gamma - Al_2O_3$ were present and mixed phases were absent; it was shown that the phase Ni_3S_2 may have been present.
2. The specific surface and adsorption volume of a $WS_2 - NiS - Al_2O_3$ catalyst were determined by the adsorption of nitrogen vapor at the temperature of liquid nitrogen and by the adsorption of toluene and benzene from their solutions in isooctane; its porous structure was characterized by the adsorption of nitrogen, and it was shown that it was nonuniformly porous: the effective radii of the pores varied from less than 10 \AA to greater than 150 \AA .
3. By comparison of the distribution of pore volume with respect to effective radius and of the specific surface accessible to nitrogen, benzene, and toluene molecules with the catalytic activities of the samples investigated, it was shown that the surface of the catalyst that is inaccessible to toluene molecules does not take part in the hydrogenation of phenol at 380° and at an initial pressure of hydrogen of 110-120 atm.

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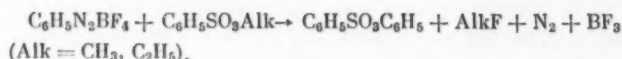
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DECOMPOSITION OF BENZENEDIAZONIUM FLUOBORATE IN BENZENESULFONIC ESTERS AND IN ACETOPHENONE

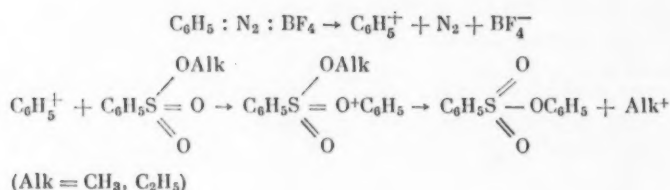
L. G. Makarova and M. K. Matveeva

In continuation of our investigations [1,2] on the demonstration of the cationoid nature of phenyl formed by the decomposition of benzenediazonium fluoborate in substitution reactions in a benzene ring containing orienting groups of the second kind we have carried out the present work on the decomposition of benzenediazonium fluoborate in benzenesulfonic esters and in acetophenone. We considered that the entry of phenyl into the meta position to a meta-orienting group (alkoxysulfonyl or acetyl) would confirm the cationoid nature of the phenyl formed by the decomposition of benzenediazonium fluoborate.

We carried out the decomposition of benzenediazonium fluoborate in methyl and ethyl benzenesulfonates, but no products in which phenyl entered the benzene ring in these esters were formed. The action of the phenyl was directed to the alkoxysulfonyl group, and in both cases the only reaction product identified was phenyl benzenesulfonate, the yield being 40% in the case of the ethyl ester and 35% in case of the methyl ester of benzenesulfonic acid:



On analogy with the transesterification of benzoic esters that occurs when benzenediazonium fluoborate is caused to decompose in them [1, 2] and on the basis of modern views on the acid hydrolysis of esters [3], the formation of phenyl benzenesulfonate must be interpreted as a proof of the action of a phenyl cation on the alkoxysulfonyl group and therefore as a proof of the heterolytic decomposition of benzenediazonium fluoborate:

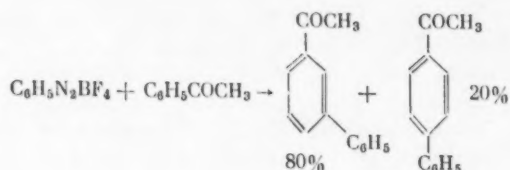


The action of the phenyl radical on a benzenesulfonic ester gives quite different products. In the decomposition of benzoyl peroxide in methyl benzenesulfonate [4] (competing attack by components of the binary mixture chlorobenzene + methyl benzenesulfonate) phenyl entered the benzene ring and, in accordance with its radical character, it entered mainly the position ortho to the methoxysulfonyl group, the meta and para derivatives being formed in approximately statistical proportions. Hence, in this case also, the phenyl from benzenediazonium fluoborate behaves differently from the phenyl radical from a homolytically decomposing source.

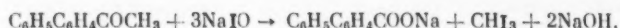
As regards the decomposition of benzenediazonium fluoborate in acetophenone it must be remembered that the acetyl group is a relatively weak meta-orienting group. Thus, in the nitration of acetophenone 68% of 3'-nitroacetophenone is formed [5]. Hence, in the action of an electrophilic reagent on acetophenone, though

the m-isomer is formed preferentially, the o- and p-isomers may also be formed.

In the decomposition of benzenediazonium fluoborate in acetophenone phenyl entered mainly in the m-position to the acetyl group, but at the same time some of the p-isomer was formed:



We isolated 3'- and 4'-phenylacetophenones; also, part of the mixture of phenylacetophenones was subjected to the iodoform reaction:



The mixture of 3- and 4-biphenylcarboxylic acids was separated by taking advantage of the differing solubilities of their sodium salts, and the acids obtained were identified. By this method we confirmed the predominant formation of the m-isomer. The ratio of the amounts of m- and p-isomers formed was 4 : 1. Also, among the reaction products we found 1,3,5-triphenylbenzene, a polymerization product from acetophenone formed, evidently, under the action of boron trifluoride.

Hence, also in the case of the relatively weak m-orienting acetyl group, phenyl preferentially enters the m-position and so differs in behavior from the phenyl arising from a homolytically decomposing source of phenyl: in the decomposition of potassium phenylazoformate in acetophenone no substitution of phenyl in the benzene ring occurred, the reaction product being the dimer of the $\text{CH}_2\text{COC}_6\text{H}_5$ radical (1,4-diphenyl-1,4-butanedione)[6]. Hence, the reaction with acetophenone again confirms the cationoid nature of the phenyl from benzenediazonium fluoborate and the heterolytic character of the decomposition of the diazonium salt.

EXPERIMENTAL

Decomposition of Benzenediazonium Fluoborate in Methyl Benzenesulfonate. Over a period of 90 minutes 92 g (1 molecular proportion) of benzenediazonium fluoborate was added to 165 g (2 molecular proportions) of methyl benzenesulfonate heated to 70–80°. The mixture was then kept for 45 minutes at the same temperature. On the next day the mixture was diluted with ether, and the solution was washed with 10% NaOH and with water and was dried with sodium sulfate. Ether was distilled off, and vacuum distillation of the residue gave:

Fraction I	b.p. 122–127° (4 mm);	111.8 g
Fraction II	b.p. 152–170° (4 mm);	49.2 g
Fraction III	b.p. 175–210° (4 mm);	4.4 g

Fraction I was methyl benzenesulfonate. Fraction II solidified and was crystallized from ethanol; m.p. 34–35° (m.p. of phenyl benzenesulfonate 34–35° [7]). Yield 34.3%.

Found % C 61.90; 61.79; H 4.35; 4.20; S 13.75; 13.83; $\text{C}_{12}\text{H}_{10}\text{O}_3\text{S}$. Calculated %: C 61.53; H 4.30; S 13.69.

Fraction III was an oil, neutral to litmus, which did not solidify on standing. The whole of Fraction III was boiled with 10% KOH solution in methanol for six hours. Alcohol was distilled off, the residual salt mixture was dissolved in water; the solution was washed with ether, and water was distilled off. The residue was dried and extracted in an extraction apparatus with absolute ethanol. The residue after the removal of alcohol was heated with two parts of potassium ferrocyanide, and an oil distilled off which was hydrolyzed with boiling 20% hydrochloric acid. When the acid solution was cooled, a precipitate formed, and this redissolved when the mixture

was made alkaline with aqueous sodium hydroxide. The mixture was acidified and extracted with ether. Ether was distilled off, and the residue was sublimed. The melting point of the product, alone and in admixture with benzoic acid, was 122°.

Decomposition of Benzenediazonium Fluoborate in Ethyl Benzenesulfonate. Over a period of 1 hour 20 minutes 77 g (1 molecular proportion) of benzenediazonium fluoborate was added to 150 g (2 molecular proportions) of ethyl benzenesulfonate at 70-75°. The mixture was kept at 80° for one hour and then treated as in the case of methyl benzenesulfonate. Vacuum fractionation gave:

Fraction	I	b.p. 136-145° (6 mm); 73 g
Fraction	II	b.p. 147-150° (3 mm); 36.1 g
Fraction	III	b.p. 185-210° (6 mm); 2.3 g

Fraction I was ethyl benzenesulfonate. Fraction II solidified. It was crystallized from ethanol, and its melting point, alone and in admixture with the phenyl benzenesulfonate from the previous experiment, was 34-35°. Yield 39.5%. Fraction III was an oil, neutral to litmus. When treated as Fraction III of the preceding experiment it gave only benzoic acid.

Decomposition of Benzenediazonium Fluoborate in Acetophenone. Over a period of two hours 170 g (1 molecular proportion) of benzenediazonium fluoborate was added in small portions with mechanical stirring to 325 ml (3 molecular proportions) of acetophenone heated in an oil bath to 60° (initial temperature). The addition of the diazonium salt raised the temperature to 80°; the reaction mixture turned red. When the addition was complete the mixture was stirred at 80-85° for one hour. The mixture was dissolved in ether, and the solution was washed with 10% NaOH solution and with water; it was dried with sodium sulfate, and ether was distilled off. Vacuum distillation gave:

Fraction	I	b.p. 74-82° (5 mm)
Fraction	II	b.p. 84-240° (5 mm); 37 g
Fraction	III	b.p. 240-260° (6 mm); 30 g

Fraction I was acetophenone. Fraction III was a caramel-like red mass, most of which crystallized out when acetone was added. Crystallization from a mixture of benzene and ligroin gave white crystals, m.p. 174°.

Found %: C 94.38; 94.25; H 5.98; 5.83 $C_{24}H_{18}$. Calculated %: C 94.09; H 5.92.

This product was 1,3,5-triphenylbenzene, for which the literature [8] gives m.p. 174°.

Vacuum fractionation of Fraction II gave Fraction I', b.p. 70-140° (3 mm), 12.5 g; Fraction II', b.p. 150-158° (3 mm), 11.5 g; Fraction III', b.p. 165-180° (2 mm), 11 g.

Refractionation of Fraction I' under reduced pressure gave acetophenone and a higher fraction, b.p. 140-145° (1 mm), which was added to Fraction II'. Fraction II' gave a reaction for ketone with sodium nitroprusside; it was converted into its semicarbazone. After crystallization from alcohol the semicarbazone melted at 208-212°. The semicarbazone was decomposed with boiling 10% hydrochloric acid, and the oil formed was extracted with ether; the extract was dried with sodium sulfate. Ether was distilled off, and there remained a partially crystallized oil. The crystals were filtered off, (Residue No. 1, Filtrate No. 1). Residue No. 1 was fractionally crystallized from methanol, and gave:

Fraction	I,	crystals of m.p. 120-121°
Fraction	II,	crystals of m.p. 119-121°
Fraction	III,	crystals melting from 95° to 110°.

Fractions I and II consisted of 4'-phenylacetophenone (for the melting point the literature [9] gives 121°). The semicarbazone of 4'-phenylacetophenone was prepared; after crystallization from aqueous pyridine it melted at 245°. Fraction III was further fractionally crystallized from methanol: some more 4'-phenylacetophenone was separated, and the last fraction, an oil which crystallized with difficulty, was added to Filtrate No. 1. Filtrate No. 1 was a semisolid mass; it distilled at 173° at a residual pressure of 6 mm. The distillate was a colorless viscous oil; n_D^{20} 1.6174. After one day crystals began to separate from the oil, and when the mass was then

stirred with a glass rod it crystallized completely; after crystallization from a large amount of heptane it had m.p. 36°.

Found % C 85.96; 85.94; 85.86; H 5.99; 6.13; 6.25 $C_{14}H_{12}O$. Calculated %: C 85.64; H 6.17.

A semicarbazone was prepared from the substance of m.p. 36°; after being crystallized from alcohol this melted with decomposition at 215°.

Found % C 71.48; 71.50; H 6.04; 6.03 $C_{15}H_{15}N_2O$. Calculated %: C 71.41; H 6.00

The phenylacetophenone of m.p. 36° was subjected to cleavage by sodium hypiodite in dioxane solution. Iodoform was separated, dioxane was distilled off, and the alkaline solution remaining was acidified with dilute hydrochloric acid; a precipitate formed and was recrystallized from heptane (colorless plates). The melting point of this substance, alone and in admixture with known 3-biphenylcarboxylic acid was 163-164°. The phenylacetophenone of m.p. 36° was therefore the m-isomer. Campaigne and Reid [10], who obtained 3'-phenylacetophenone by the Grignard reaction, isolated it in the form of an oil. When the iodoform reaction was carried out similarly with 4'-phenylacetophenone, a water-insoluble sodium salt was obtained; boiling with concentrated hydrochloric acid and crystallization from aqueous alcohol gave 4-biphenylcarboxylic acid, m.p. 222° (the literature [11] gives 222°). 3'- and 4'-Phenylacetophenones were formed in the ratio of 4 : 1.

Fraction III' was a thick red oil, which did not give a reaction for the carbonyl group; after dilution with acetone it gave some 1,3,5-triphenylbenzene. Without isolation of the isomeric phenylacetophenones, part of Fraction II was subjected to the iodoform reaction. The resulting 3- and 4-biphenylcarboxylic acids were again obtained in the ratio of 4 : 1.

SUMMARY

1. Phenyl formed by the decomposition of benzenediazonium fluoborate in methyl and ethyl benzenesulfonates acts only on the alkoxysulfonyl group in these esters and in both cases gives phenyl benzenesulfonate.
2. In the decomposition of benzenediazonium fluoborate in acetophenone, 3'- and 4'-phenylacetophenones are formed in the ratio of 4 : 1.
3. These reactions constitute proof of the heterolytic character of the decomposition of benzenediazonium fluoborate.

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CATALYTIC DEHYDROGENATION OF n-PENTANE AT VARIOUS TEMPERATURES

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We have previously reported [1,2] that an alumina-chromia catalyst promoted by potassium oxide ($Al_2O_3 : Cr_2O_3 : K_2O = 90.7 : 5.6 : 3.7$ mole per cent) is very effective in the dehydrogenation of n-pentane and isopentane. At 527° we obtained n-pentane catalyzates containing 30-31% of pentenes and isopentane catalyzates containing up to 38% of isopentenenes. In these experiments the catalyst was first heated to 527° in a stream of air, which was then displaced with nitrogen; a little (about 2 ml) of the original hydrocarbon was then passed in order to fill the system with its vapor and level out the temperature. As our further investigations showed, the activity of the catalyst increases considerably if, after the carbonaceous film is burnt off the catalyst surface in atmospheric oxygen, a treatment with hydrogen is given.

Maslianskii and Bursman [3] showed that a reduced alumina-chromia catalyst is more active in the dehydrogenation of cyclohexane than an oxidized catalyst. In this respect the temperature at which the catalyst is treated with atmospheric oxygen and hydrogen is of great importance. In the papers of Voltz and Weller [4] there are also references to the different behavior of oxidized and reduced alumina-chromia catalysts with respect to electric conductivity, catalytic activity (hydrogen-deuterium exchange and decomposition of hydrogen peroxide), and poisoning with water.

In the present work we carried out the catalytic treatment of n-pentane in presence of a catalyst that had received a preliminary treatment with atmospheric oxygen and hydrogen; the conditions were more or less standard. The object of the present investigation was the study of the effect of temperature on the dehydrogenation of n-pentane over an alumina-chromia-potassia catalyst and comparison of the results with the equilibrium concentrations of pentenes in this reaction. In all experiments we drew up a molar balance of the reaction and determined the relation between catalyst selectivity and temperature.

EXPERIMENTAL

In these experiments we used the same catalyst as in the preceding investigation [2] (30 ml; 19.1 g; length of catalyst layer 90 mm; internal diameter of tube 18 mm). The catalyst was first heated in a stream of air to a temperature 3-5° higher than that of the experiment. Then, after displacement of the air with nitrogen (20 minutes), the catalyst was treated with hydrogen for 90 minutes. n-Pentane (b.p. 36.0-36.5° (760 mm); n_D^{20} 1.3577; d_4^{20} 0.6263) was then passed into the system from a spray buret at a space velocity of 0.5 hour⁻¹. In this series of experiments the reaction was carried out for about one hour and the catalyzate and gas were collected during the last 43-44 minutes; before the experiment about 2.4 g of pentane was passed over the catalyst, and during the experiment 6.27 g was passed. Then, after displacement of reaction products and hydrogen from the system with nitrogen (20 minutes), the catalyst was treated with air in order to burn off the "coke" (45-50 minutes). The water formed was absorbed with anhydrous calcium chloride, and the carbon dioxide was absorbed with ascarite. The stream of air passing through the system was regulated in such a way that the temperature of the catalyst did not exceed 600°. From these data we determined the composition of the "coke". In each experiment we made an approximate estimate of the gravimetric balance, which gave a gross total ranging from 98 to 102%, which indicates that the experimental procedure and method of trapping the reaction products were quite satisfactory. Table 1 gives the properties of the liquid catalyst and composition of the gas at various temperatures.

TABLE 1

Effect of Temperature on the Properties of the Liquid Catalyzate and the Composition of the Gas

Expt. no.	Temperature (°C)	Yield of liquid catalyzate (% by wt)	Amount of gas (liters at STP)	Properties of catalyzate			Composition of gas (%) by volume			Carbon value	Composition of "coke"
				n_D	Iodine value	Content of pentenes (% by wt)	H ₂	C _n H _{2n}	C _n H _{2n+2}		
1	450	99,6	0,182	1,3600	35,3	9,0	99,2	0,2	0,6	—	C _{2,0} H ₁
2		99,6	0,180	1,3600	35,2	9,0	99,8	0,2	0,0	—	C _{2,0} H ₁
3	475	97,6	0,545	1,3622	72,7	20,0	93,0	0,9	6,1	1,8	C _{1,0} H ₁
4		98,4	0,505	1,3620	70,7	19,5	92,2	0,6	7,2	—	C _{1,0} H ₁
5	500	92,0	0,950	1,3600	126,3	34,5	90,7	1,0	8,3	1,8	C _{2,0} H ₁
6		92,6	1,007	1,3655	122,9	33,8	90,5	1,0	8,5	—	C _{1,4} H ₁
7	527	84,4	1,811	1,3710	156,4	43,1	78,5	2,8	18,7	—	C _{2,0} H ₁
8		85,7	1,760	1,3705	158,7	43,6	82,9	2,0	15,1	1,8	C _{2,0} H ₁
9	550	77,0	2,357	1,3740	193,1	53,2	75,8	4,7	19,5	—	C _{2,3} H ₁
10		76,4	2,339	1,3745	195,0	53,7	69,2	6,7	24,1	1,7	C _{2,7} H ₁

• The iodine value was determined by Gal'pern's bromometric method [5].

TABLE 2

Effect of Temperature on Yield of Reaction Products and on Catalyst Selectivity

Temperature of experiment (°C)	Un-changed C ₅ H ₁₂	C ₅ H ₁₀ formed	Amount of pentane converted into		Total in molar balance	Selectivity
			"coke"	gas		
450	91	9	0	0	100	100
475	78	20	2	1	101	92
500	61	32	4	2	99	84
527	48	38	10	6	102	75
550	36	42	13	10	101	65

The molar balance can be calculated approximately from a knowledge of the yield of liquid catalyzate, its content of unsaturated hydrocarbons, the group analysis of the gas, the carbon value (the number of volumes of CO₂ formed in the burning of one volume of gaseous methane hydrocarbons), and the composition of the "coke". In this it was assumed that the gas did not contain olefins. In practice they are formed only in small amounts. The extent of gas formation was calculated from the equation:

$$P_r = \frac{G \cdot \alpha}{5},$$

in which P_r is the amount of pentane (mole %) converted into gaseous hydrocarbons, G is the sum of saturated and unsaturated hydrocarbons in the gas (mole %), and α is the carbon value.

The extent of coke formation was determined by the equation:

$$P_k = \frac{2 \left[H_R + G \left(1 - \frac{\alpha}{5} \right) \right]}{12 - \frac{5}{y}},$$

in which P_k is the amount of pentane (mole %) converted into "coke", H_k is the amount of hydrogen (mole %) liberated from the "coke", G and α are the same as in the preceding equation, and y is the number of C atoms per H atom in the composition of the "coke" (C_yH_1).

$$\text{Selectivity (mole \%)} = \frac{C_5H_{10} \text{ formed (moles)}}{C_5H_{12} \text{ decomposed (moles)}} \cdot 100$$

The results on catalyst selectivity and molar balance are given in Table 2 and Figures 1 and 2.

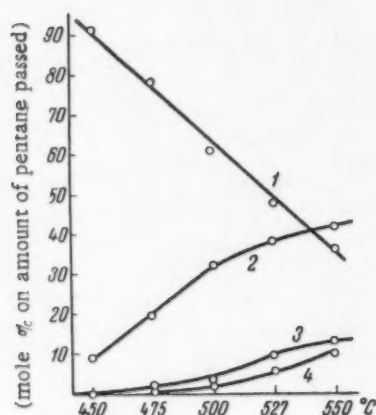


Fig. 1. Effect of temperature on the molar balance of reaction products: 1) pentane; 2) pentenes; 3) "coke"; 4) gas.

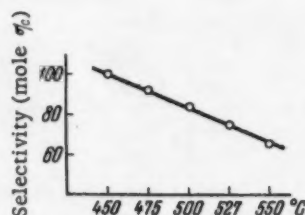


Fig. 2. Effect of temperature on catalyst selectivity.

Equilibrium Concentrations of Pentenes. From the free energies of formation of all the isomeric pentenes [6] we calculated equilibrium constants for the dehydrogenation of n-pentane (K_p), and from the equation

$$K_p = \frac{x^2}{1-x^2} \quad (1)$$

we calculated the corresponding yields of pentenes (x). The results are presented in Table 3.

TABLE 3
Thermodynamic Calculation for the Dehydrogenation Reaction Pentane \rightleftharpoons Pentenes

Hydrocarbon	600°K (327°C)		700°K (427°C)		800°K (527°C)		900°K (627°C)	
	K_p	x	K_p	x	K_p	x	K_p	x
1-Pentene	0,00007	0,8	0,00286	5,3	0,04854	21,5	0,44703	55,6
cis-2-Pentene	0,00029	1,7	0,00922	9,6	0,12236	33,0	0,93510	69,5
trans-2-Pentene	0,00030	1,7	0,00902	9,5	0,12013	32,7	0,90426	68,9
All pentenes	0,00066	2,6	0,02110	14,4	0,29103	47,5	2,28639	83,4

As our experiments showed, the dehydrogenation of pentane is accompanied by side reactions, namely cracking with formation of gaseous hydrocarbons, and the deposition of a "carbonaceous film" (for brevity we have called this deposit "coke") on the catalyst with simultaneous liberation of hydrogen.

From the formula *

$$h_p = \frac{x(n_3 - n_2 + x)}{(n + n_2 - x)(\sum n_i - n_2 + x)} \quad (2)$$

* The method given for the calculation, and also for the drawing up of the molar balance, was suggested by I. I. Levitskii.

we calculated the theoretical yields of all the pentenes, account being taken of side reactions. For this purpose in each experiment we determined the composition of the reaction mixture in moles of reaction products per mole of original pentane, the various amounts being n_1 (unchanged pentane), n_2 (pentenes), n_3 (hydrogen), n_4 (gaseous hydrocarbons), and $\Sigma n_i = n_1 + n_2 + n_3 + n_4$. In Table 4 and Fig. 3 we give the experimental yields of pentenes and their equilibrium concentrations calculated from Equations (1) and (2). The values of K_p (Column 8) were determined graphically from the data in Table 3.

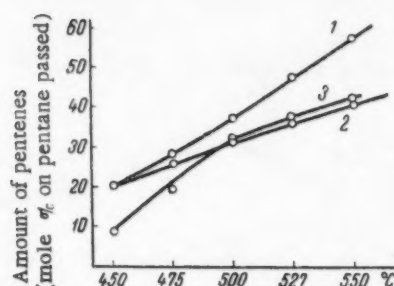


Fig. 3. Equilibrium and experimental yields of pentenes as a function of temperature: 1) equilibrium concentrations according to Equation (1); 2) equilibrium concentrations according to Equation (2); 3) experimental yields.

The results show that at 450° and 475° the catalyst has low activity: in the first case 50% of the equilibrium yield of pentenes is obtained, and in the second case 73%; the selectivity is high (100% and 92%, respectively). At 500-550° the catalyst becomes more active and the dehydrogenation reaction of pentane practically attains equilibrium. As side reactions become more prominent with rise in temperature (at 500° 6 mole per cent of pentane is converted into gas and "coke", and at 550° 23 mole per cent of the pentane undergoes this change), the selectivity of the catalyst falls from 84% at 500° to 65% at 550°. It is this that explains the discrepancy between Curve 1, on the one hand, and Curves 2 and 3, on the other (Fig. 3). A notable fact following from Fig. 3 is that, in the transformations of pentane over the given catalyst, "coke" is formed to a considerably greater extent than gas.

TABLE 4
Experimental and Equilibrium Yields of Pentenes at Various Temperatures

Expt. no.	Temperature (°C)	Yield (mole fraction, on amount of pentane passed)					K_p	Equilibrium concentrations of pentenes (x)	
		C_5H_{12} n_1	C_5H_{10} n_2	H_2 n_3	gas n_4	Σn_i		according to Eq. (1)	according to Eq. (2)
1	450	0,907	0,092	0,093	0	1,092	0,04285	0,203	0,203
2		0,907	0,092	0,093	0	1,092		0,203	0,203
3	475	0,783	0,200	0,259	0,019	1,261	0,08511	0,280	0,257
4		0,793	0,197	0,237	0,027	1,254		0,280	0,266
5	500	0,603	0,326	0,438	0,046	1,413	0,15766	0,369	0,316
6		0,612	0,322	0,467	0,049	1,450		0,369	0,310
7	527	0,474	0,381	0,729	0,200	1,784	0,29103	0,475	0,359
8		0,482	0,384	0,747	0,154	1,767		0,475	0,357
9	550	0,361	0,420	0,916	0,293	1,990	0,48420	0,571	0,403
10		0,354	0,422	0,830	0,369	1,975		0,571	0,416

The results enable us to conclude that, in order to increase the yields of pentenes in the range 500-550°, it is not the activity of the catalyst that must be increased, but its selectivity.

SUMMARY

1. An investigation was made of the effect of temperature on the course of the dehydrogenation of n-pentane in presence of an alumina-chromia-potassia catalyst.

2. It was shown that at 500-550° under the given conditions and for a given extent of side reactions dehydrogenation of n-pentane attains an equilibrium state.

3. It was shown that, in order to increase the yield of pentenes, it is not the activity of the catalyst that must be increased, but its selectivity.

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ISOMERIZATION OF SATURATED HYDROCARBONS
COMMUNICATION 2. ISOMERIC TRANSFORMATIONS
OF $C_{12} - C_{16}$ PARAFFINS

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The use of multifunctional catalysts has enabled us to solve the problem of the isomerization of saturated hydrocarbons boiling up to 150° [1] and has created objective prerequisites for the study of the isomeric transformations of hydrocarbons of higher molecular weight. Nevertheless, the isomerization of paraffins boiling above 200° in presence of heterogeneous catalysts is associated with considerable difficulties, of which the greatest is undoubtedly the occurrence of much cracking of the hydrocarbons undergoing isomerization. It is probably impossible to avoid cracking (in the present case, hydrocracking) during the isomerization of hydrocarbons of fairly high molecular weight, for both the isomerization and decomposition reactions of hydrocarbons proceed at the same active centers. Only by choosing optimum conditions is it possible to minimize the destruction of the starting material and obtain a yield of 40-60% of branched paraffins of b.p. above 200° . In the solution of this problem in its application to the isomerization of paraffins of high molecular weight, the selection of special catalysts is the principal and most difficult problem.

The platinumized alumina-silica catalyst used in work on the isomerization of paraffins of lower molecular weight was found to be unsuitable because of its high cracking power. An attempt to use platinumized alumina-silica the specific surface of which had been reduced to 100 sq. m/g by treatment with steam was also unsuccessful, for this catalyst was found to have low activity. Reduction of the platinum content of the catalyst to about 0.1% was also ineffective, for the catalyst prepared in this way was found to have low activity, not only in hydrocracking, but also in isomerization reactions. Somewhat better results were obtained in presence of platinumized alumina activated with hydrogen fluoride. It must be pointed out that catalysts based on alumina required higher reaction temperatures than alumina-silica catalysts. Thus, HF-treated alumina containing 0.5% Pt brought about the same degree of isomerization in n-heptane at 410° as platinumized alumina-silica did at 370° . Despite the higher temperature, the selectivity of platinumized alumina was found to be somewhat higher than that of platinumized alumina-silica. Thus, in the isomerization of n-dodecane over this catalyst at 410° and 10 atm we obtained about 50% of branched C_{12} paraffins with a total yield of liquid products of 80%, whereas over a platinumized alumina-silica catalyst at only 350° we obtained only 30% of uncracked C_{12} fraction. Some reduction in the specific surface of the alumina has a favorable effect on the selectivity of catalysts based on it. However, a catalyst prepared from an alumina of very high bulk density (0.85 g/ml; 140 sq.m/g) was found to have low activity, so that great reduction in the specific surface of catalysts may even be detrimental.

Of the other factors, pressure has an appreciable effect on selectivity with respect to isomerization. It must be stated that the effect of pressure on isomerization and hydrocracking process has not been completely elucidated, at least for hydrocarbons of high molecular weight; it is essential to continue work in this direction, for the available information is rather contradictory. In any case, the conditions selected in the present investigation are probably not optimum (this refers chiefly to the material balance) and have been determined mainly with the object of bringing about isomerization with satisfactory yields of the desired fractions under conditions comparable with those used in the study of the isomerization of $C_6 - C_8$ paraffins [1]. The difficulty of studying the effect of pressure on the isomerization of higher paraffins lies also in the impracticability of the synthesis of the starting materials in large amounts. As will be shown below, the effect of pressure on the hydrocracking and

isomerization of $C_8 - C_8$ paraffins does not always coincide with that found for paraffins on higher molecular weight. However, we may make some observations on the effect of pressure on the transformations of hydrocarbons. Essentially, pressure affects two reactions: isomerization and hydrocracking. Rise in pressure in presence of activated alumina reduces hydrocracking, and this is true for hydrocarbons of any molecular weight. As regards an alumina-silica catalyst: as already shown [1], the hydrocracking of paraffins of fairly low molecular weight (heptane) increases with rise in pressure, whereas the hydrocracking of dodecane is reduced by rise in pressure.

The effect of pressure on isomerization reactions is not altogether clear either. Thus, in processes over an alumina-silica catalyst (at least at temperatures of about 370° and higher) rise in pressure scarcely affects the extent of isomerization of hydrocarbons of any molecular weight, which is in general accord with the results of other authors [2]. On the other hand, increase in pressure in our experiments with dodecane in presence of activated alumina resulted in appreciable reduction in the amount of branched paraffins formed, whereas, both according to our results and also to other available data [3, 4], the isomerization of lower-boiling paraffins (heptane-decane) is not greatly affected by pressure. It is possible that some part is played here by the phenomenon of capillary condensation of dodecane in the pores of the catalyst. In any case, we must always take into account the fact that the temperatures required for isomerization often lie below the critical temperatures of $C_{12} - C_{16}$ paraffins (thus the critical temperature of n-dodecane is 390°). In referring to the effect of pressure on isomerization we must remember that we are here considering changes in pressure in the range 10-50 atm. The retardation of isomerization by a high pressure of hydrogen (about 500 atm) has a different chemical meaning and is readily explicable by the absence of the concentration of olefins necessary for isomerization in the equilibrium mixture $\text{alkane} \rightleftharpoons \text{alkenes} + \text{H}_2$ [5, 6]. It will be seen from these considerations that the selection of optimum conditions for the isomerization of hydrocarbons of high molecular weight is not an easy matter.

In view of the fact that, as already stated, the main object of our work was the study of the composition and properties of isomerizates obtained under conditions as close as possible to those used in the isomerization of the lower-boiling paraffins [1], we carried out the isomerization of $C_{12} - C_{16}$ paraffins at low pressures on a relatively active catalyst (alumina containing 1% of fluorine and 0.5% of platinum). The activity of such a catalyst at 410° corresponded to that of the platinumized alumina-silica used in the previous work when employed at 370° [1].

EXPERIMENTAL

The isomerization of $C_{12} - C_{16}$ paraffins was carried out in a flow system in a special apparatus intended for work under high-pressure conditions. The apparatus was described previously [1]. The catalyst was prepared as follows: alumina (bulk density 0.72 g/ml) was kept for one day in 0.1 N HF, the solution was decanted, and the catalyst was dried at $120-130^\circ$; the alumina activated in this way was treated in a solution of chloroplatinic acid containing the required amount of platinum. The absorptive power of the given sample of alumina was determined beforehand. The resulting catalyst was dried at $120-130^\circ$ and then reduced in a stream of hydrogen in a glass reaction vessel at temperatures rising to 500° . The cooled catalyst was transferred to the steel reactor of the apparatus, in which it was again heated to 500° , this time in presence of hydrogen under pressure.

The isomerization experiments were carried out at the following hydrogen pressures: 10 atm for C_{12} paraffins, tridecane, and tetradecane; 8 atm. for pentadecane; and 6 atm for hexadecane. The temperature of the experiments was 400° (with the exception of the experiments with dodecane and 2-methylundecane, which were carried out at 410°). In all experiments the space velocity was 1.0 hour^{-1} , and the molar ratio hydrogen:hydrocarbon was 4. The analysis of the isomerizates was in the main carried out as in the case of alkenes of high molecular weight [7].

The main criteria used in judging the structures of the hydrocarbons obtained in the isomerization were their infrared absorption spectra and freezing points. The following sequence of operations was employed in the analysis of isomerizates. The catalyzate was distilled completely from a Favorskii flask; low-boiling fractions, boiling below the isomers of the original hydrocarbon, were distilled off through a column. The residue, which corresponded in boiling point to isomers of the original hydrocarbon, was characterized by its main properties (molecular weight, infrared spectra, freezing point, etc.). Since the catalyzates obtained in the isomerization of n-alkanes generally contained 20-30% of the original hydrocarbons, these were first removed by treatment with dry urea by known methods. An analogous analysis of a catalyzate was recently used by Minachev

Shulkin in work on the isomerization of n-decane [3]. We have previously published a detailed description of the procedure for determining the average degree of branching of paraffins from infrared absorption spectra [8].

In the present work we again verified the ratios of optical densities in the region $3.35-3.51 \mu$ $\frac{I_{3.42}}{I_{3.38}} ; \frac{I_{3.51}}{I_{3.38}}$

for 30 pure $C_{12}-C_{16}$ paraffins of various degrees of branching. These values $\frac{I_{3.42}}{I_{3.38}} ; \frac{I_{3.51}}{I_{3.38}}$, in which account

was taken of the actual molecular weights of the hydrocarbons mixtures investigated, were used also in the determination of the average degrees of branching of the isomerizates obtained.

We must discuss the material balance in the experiments on the isomerization of $C_{12}-C_{16}$ paraffins. As stated above, hydrocracking is here fairly significant and it is almost impossible to avoid this phenomenon. However, as hydrocracking proceeded mainly in the middle parts of molecules, the yields of liquid products were fairly high and attained 80-90%. Because of the relatively high losses in the fractionations, the yields of hydrocarbons of molecular weight equal to that of the original hydrocarbon were difficult to estimate exactly; in any case they comprised not less than half of the total liquid products, i.e. 40-50% on the original hydrocarbon. Because of the low pressures, lower yields of the desired products were obtained in the experiments with pentadecane and hexadecane. The hydrocarbons used were synthesized by Grignard and Grignard-Wurtz reactions. The intermediate products of the synthesis, tertiary alcohols, were dehydrated over pure alumina at 280-300° at a residual pressure of 10 mm. The olefins were then hydrogenated in an autoclave over Raney nickel at 150-170° and 100-120 atm. The properties and methods of preparation of the hydrocarbons are given in Table 1. The results of the isomerization of nine individual paraffins are given in Table 2.

TABLE 1

Properties and Methods of Preparation of Paraffins

Paraffin	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Method of preparation
Dodecane	103.5 (18.5) (212°)	1.4211	0.7501	From nonylmagnesium bromide and allyl bromide
2-Methylundecane	95 (16) (200°)	1.4207	0.7473	From nonylmagnesium bromide and acetone
5-Methylundecane	96 (18) (196°)	1.4227	0.7512	From hexylmagnesium bromide and 2-hexanone
2,4-Dimethyldecane	87 (17.5) (188°)	1.4195	0.7468	From hexylmagnesium bromide and 4-methyl-2-pentanone
2,5,8-Trimethylnonane	87 (22) (182°)	1.4182	0.7462	From isopentylmagnesium bromide and ethyl acetate
Tridecane	114 (13) (232°)	1.4258	0.7574	From decylmagnesium bromide and allyl bromide
Tetradecane	123.5 (11) (250°)	1.4288	0.7630	From decylmagnesium bromide and butyraldehyde
Pentadecane	134.5 (9) (270°)	1.4313	0.7691	From propylmagnesium bromide and lauraldehyde
Hexadecane	145.5 (8.5) (288°)	1.4342	0.7744	From nonylmagnesium bromide and heptanal

*Boiling points calculated for atmospheric pressure are given in parentheses.

Before we proceed to a discussion of the results, we shall discuss the thermodynamic possibilities of isomeric transformations of paraffins of the given molecular weight. As there are no experimental or calculated values of free energies of hydrocarbons of such high molecular weight, apart from n-alkanes, we were obliged to make use of the corresponding data for compounds of low molecular weight in our calculations for equilibrium mixtures. It must be stated that such extrapolation is not only valid, as was shown in Tatevskii's researches [9,10], but can, in our opinion, give with certain corrections values that are not less accurate than those given by experimental thermodynamic measurements of the properties of paraffins of high molecular weight. The experimental data on C_6-C_8 paraffins indicate that isomerization proceeds mainly in the direction of the formation of mono- and di-methyl alkanes. The equilibrium composition calculated from thermodynamic data for

these hydrocarbons only was conditionally called by us the "realizable-equilibrium composition" [1].

We shall now calculate the "realizable-equilibrium composition" for paraffins of high molecular weight. There is no need to prove that for C_{12} and higher paraffins calculations of the equilibrium concentrations of all theoretically possible isomers is practically impossible, but there is no particular necessity for this calculation. We need only calculate the concentrations of the normal, monomethyl, and dimethyl paraffins actually formed and also, if necessary, of some particular group of hydrocarbons having a structural feature in common.

TABLE 2
Properties of Isomerizates from $C_{12}-C_{16}$ Paraffins

Original hydrocarbon	Boiling limits (°C)	n_D^{20}	d_4^{20}	Mol. wt. *	Freezing point (°C) **	Comp. acc. to infrared spectrum *** (%)		Amount removed by urea (%)
						mono-substituted	di-substituted	
2-Methylundecane	180-200	1,4453	0,7871	150	-77	50	50	—
5-Methylundecane	180-205	1,4345	0,7704	159	-64	50	50	—
2,4-Dimethyldecane	180-205	1,4327	0,7677	165	-70	0	100	—
2,5,8-Trimethylnonane	170-200	1,4349	0,7712	159	-80	0	100	—
Dodecane	180-210	1,4337	0,7697	159	-82 (-30)	20	80	17
Tridecane	195-225	1,4323	0,7678	171	-84 (-25)	20	80	30
Tetradecane	210-245	1,4368	0,7755	187	-84 (-15)	10	90	34
Pentadecane	225-260	1,4442	0,7868	197	-79 (-15)	0	100	32
Hexadecane	240-277	1,4532	0,8008	201	-72 (-5)	0	100	27

* The molecular weights refer to the branched hydrocarbons of the catalyzate.

** The values in parentheses are freezing points before treatment with urea.

*** After treatment with urea.

For C_6-C_8 paraffins the values of the isomerization-equilibrium constants K_p of n-alkanes, calculated by Rossini [11] and verified experimentally, are given in Table 3.

TABLE 3
Equilibrium Constants for the Isomerization of Alkanes into the Isomers Indicated

Isomer	227°C (500°K)	327°C (600°K)	427°C (700°K)
2-Methylpentane	1,96	1,57	1,2
2-Methylhexane	1,94	1,65	1,34
2-Methylheptane	2,11	1,60	1,33
3-Methylpentane (symm.)	0,95	0,79	0,70
3-Methylhexane	2,3	2,17	1,87
3-Methylheptane	2,27	1,90	1,68
4-Methylheptane (symm.)	0,74	0,61	0,54
2,4-Dimethylpentane (symm.)	1,1	0,6	0,4
2,4-Dimethylhexane	1,82	0,12	0,81
2,5-Dimethylhexane (symm.)	1,77	0,96	0,63

Note. There are now new corrected values of the free energies of paraffins [12]. In view of the fact that the corrections apply mainly to the free energies of n-alkanes, use of the new data in the calculations given below will result in only very small changes in the direction of increased concentrations of n-alkanes in the equilibrium mixtures. However, the absolute values of K_p for the isomerization of n-alkanes into branched hydrocarbons will be appreciably lower.

In practice, in the isomerization of any n-alkane of high molecular weight there will be formed both monomethylalkanes having the methyl side group in various positions and also polymethylalkanes, mainly dimethylalkanes having the methyl side groups in various positions. In our further considerations we shall not take account of the formation of trimethyl-substituted and more highly branched alkanes, because the formation of products of such structure was not detected in the catalyzate, it being found, on the contrary, that trimethylalkanes tend to pass into dimethyl-substituted isomers.

It can be seen from Table 1 that K_p for the isomerization of n-alkanes into hydrocarbons of like structural forms, e.g. 2-methylalkanes, 3-methylalkanes, etc., are fairly close in value, which gives grounds for the extrapolation of these values of K_p also to alkanes of higher molecular weight. Such extrapolation indicates that, beginning from a certain molecular weight in a series of hydrocarbons of like structure, transition from a lower homolog to a higher causes the same increase in the value of ΔZ_T^0 for all alkanes. This is valid on the condition that the introduction of a new CH_2 group in the transition T to the next homolog occurs in the main chain at a sufficient distance from the existing branchings. According to Tatevskii, for the values of ΔH_T^0 satisfactory results are obtained already when the added methylene group is attached to a carbon atom in the β -position to the branching.

In view to the fact that the entropy factor (ΔS_T^0) is more sensitive to changes of structure, then an identical change in ΔZ_T^0 in transition to the next homolog can be expected (and then only within a certain approximation) when the new methylene group is added to a carbon atom that is not closer than the γ -position to the branchings. Moreover, it is always necessary to make sure that the transition from one homolog to another is not accompanied by change in the general symmetry of the molecule, because such change greatly changes the value of ΔS_T^0 , and therefore of ΔZ_T^0 . Hydrocarbons of symmetrical structure include 3-methylpentane, 2,4-dimethylpentane, 2,5-dimethylhexane, and 4-methylheptane.

In practice, for the values of K_p in the isomerization of n-alkanes into 2- and 3-methylalkanes we may use the corresponding data for n-octane. For K_p in the isomerization of n-alkanes into 4- and 5-methylalkanes and into alkanes having a methyl side group in a more central position (incidentally, on our view the values of K_p for the isomerization of these alkanes should be close together) it is not possible to use data for 4-methylheptane, because this hydrocarbon is symmetrical. On the view that in transitions from 3- to 4-methylalkanes etc. the values of ΔH_T^0 do not change (in accordance with Tatevskii) and change in the value of ΔZ_T^0 is probably very slight, in the further treatment we shall use the value of K_p for the isomerization of n-octane into 3-methylheptane for K_p for the isomerization of n-alkanes into 4-, 5-, and 1-methylalkanes.

Let us pass now to the value of K_p for dimethylalkanes. In the order of increasing thermodynamic stability (reduction in ΔZ_T^0), all hydrocarbons of the given structural type can be divided into three groups.

1. Alkanes having vicinal methyl side groups. As the free energies of these alkanes are relative high, the formation of hydrocarbons of this structural form during isomerization will not be taken into account in our further considerations. On the same grounds we shall leave gem-dimethylalkanes out of consideration.

2. Alkanes having methyl side groups in the β -position to one another. For the value of K_p for isomerization into alkanes of this structure we may use K_p for the isomerization of octane into 2,4-dimethylhexane; in view of the fact that in the isomerization of hydrocarbons of higher molecular weight there will be a predominance (due to purely statistical reasons) of isomers in which the methyl side groups occupy more central positions, the average value of K_p for the isomerization of n-alkanes into β -dimethylalkanes must be rather high (by about 5-7%) as compared with K_p for the isomerization of the corresponding C_8 paraffins.

3. The third, most important, group consists of dimethylalkanes in which the methyl side groups are in the γ -position or still further removed from one another. There is now no longer appreciable interaction between the methyl side groups. The value of K_p for isomerization into these paraffins can be calculated from K_p for the isomerization of octane into 2,5-dimethyloctane, account being taken, of course, of the correction for the symmetry effect. The change in isobaric potential in passage from an n-alkane to a 2,5-dimethylalkane can be estimated approximately as follows: $\Delta(\Delta Z_T^0) = \Delta Z_T^0$ of 2,5-dimethylhexane - ΔZ_T^0 of n-octane - [$(\Delta Z_T^0$ of n-octane - ΔZ_T^0 of 2,4-dimethylhexane) - (ΔZ_T^0 of n-heptane - ΔZ_T^0 of 2,4-dimethylpentane)], i.e. the change in isobaric potential in the isomerization of n-alkanes into γ -dimethylalkanes is equal to the change in isobaric potential in the isomerization of n-octane into 2,5-dimethylhexane minus the absolute difference in the isobaric potentials in the isomerizations of two n-alkanes into structurally similar dimethylalkanes of

which one has a symmetrical structure. On the basis of this change in ΔZ_T^0 we calculated K_p for the isomerization of n-alkanes into 2,5-dimethylalkanes, and to this type of dimethylalkane we referred also 2,6-, 2, 7-, 3,6-, 4,7-, and other dimethylalkanes, the values of K_p of which were equated to that for isomerization into 2,5-dimethylalkanes. All these dimethylalkanes are conventionally referred to as γ -dimethylalkanes. On the basis of all these considerations we arrived at the following average values of K_p for the isomerization of $C_9 - C_{16}$ n-alkanes (Table 4).

TABLE 4
Average Values of K_p for the Isomerization of $C_9 - C_{16}$ n-Alkanes Into the Isomers Indicated

Isomers	227 °C (500 °K)	327 °C (600 °K)	427 °C (700 °K)
2-Methylalkanes	2,0	1,6	1,3
3-Methylalkanes and the other monomethyl- alkanes (except symmetrical forms)	2,3	1,9	1,7
2,4-and the like dimethylalkanes (except symmetrical forms)	1,9	1,2	0,9
2,5-, 2,6-, 3,6-, 4,8-, and the like dimethyl- alkanes (except symmetrical forms)	2,8	1,8	1,3

Further, on the basis of the average values of K_p given in Table 4, taking into account the actually occurring monomethyl- and dimethyl-alkanes having 8-16 carbon atoms we calculated the "realizable-equilibrium composition" for the isomerizates of $C_8 - C_{16}$ paraffins (Table 5). Except in the case of C_8 paraffins, the formation of hydrocarbons having symmetrical structures was not taken into account in the calculation.

TABLE 5
Realizable-equilibrium Concentrations of Higher Paraffins (%)

	227 °C (500 °K)			327 °C (600 °K)			427 °C (700 °K)			Structural forms
	normal	mono- methyl	dimethyl	normal	mono- methyl	dimethyl	normal	mono- methyl	dimethyl	
C_8 paraffins	10	53	37	14	58	28	17	59	24	Monomethyl (M): 2-, 3-, 4-methyl Dimethyl (D): 1 β , 1 γ
C_9 paraffins	8	54	38	11	58	31	13	60	27	M: 2-, 3-, 4-methyl D: 1 β , 1 γ
C_{10} paraffins	6	40	54	8	44	48	10	47	43	M: 2-, 3-, 4-methyl D: 2 β + 2 γ
C_{12} paraffins	3	27	70	4	33	63	6	36	58	M: 2-, 3-, 4-, 5-methyl D: 3 β , + 6 γ
C_{16} paraffins	1	14	85	2	18	80	2	23	75	M: 2-, 3-, 4-, 5-, 6-, 7-methyl D: 5 β + 25 γ

For Table 5 it will be seen that in the isomerization of paraffins of high molecular weight (C_{12} and higher) the predominating structural forms are dimethyl-substituted hydrocarbons, whereas the concentrations of n-alkanes are very low. From a comparison of the experimental and calculated values it is readily seen that the experimental data on the isomerization of $C_{12} - C_{16}$ alkanes (Table 2) correspond in the main with the calculated values. Thus, we could scarcely detect the formation of n-dodecane in the isomerizates of 2- and 5-methylundecanes. The infrared spectra of most of the isomerizates also indicated definitely that dimethylalkanes predominated. This is indicated also by the extremely low freezing points of the isomerizates: among hydrocarbons of the given molecular weight such low freezing points are possessed only by dimethylalkanes. Unfortunately, we can say very little about the positions of the methyl side groups in the main chain; it is probable

that there is some predominance of branched paraffins with the more central positions of branching, which is indicated by the low freezing and glass points of the pentadecane and hexadecane isomerizates. Some tentative data on the freezing points of individual paraffins are given below:

2,4-Dimethyldodecane:	- 55°	Crystallizes
3,5-Dimethyldodecane:	- 75°	Vitrifies
2,4-Dimethyltridecane:	- 49°	Crystallizes
2,4-Dimethyltetradecane:	- 35°	Crystallizes
7,8-Dimethyltetradecane:	- 70°	Vitrifies

It is interesting to compare the results on the isomerization of C_{12} - C_{16} paraffins with those on the isomerization of the corresponding olefins [7]. In the case of olefins, the isomerization of normal hydrocarbons is more rapid than in the case of paraffins, for the isomerizates of olefins contain practically no n-alkenes, whereas the content of n-alkanes in paraffin isomerizates attains 20-30%. However, further isomerization and formation of dimethyl compounds proceed more rapidly in the case of alkanes (60-80%) than in the case of the corresponding alkenes (30-40%), and it is doubtful whether this last fact is determined by thermodynamic considerations. In general, in the isomerization of alkanes of any molecular weight the calculated equilibrium concentrations are considerably more readily attained than in the isomerization of alkenes. For example, the highly branched hydrocarbon 2,5,8-trimethylnonane passes into dimethylalkanes, whereas the corresponding alkene preserves its structure unchanged. 5-Methylundecane forms up to 50% of disubstituted alkane, whereas the corresponding alkene remains almost unchanged, etc. It may be stated also, as a general rule, that the isomerizates from alkanes are more varied in composition. This is probably to be explained by the fact that in the case of alkanes the double bond may arise at almost any point of the hydrocarbon chain, so that a methyl side group may also arise at any point.

Our general views concerning the isomerization of alkanes proceeding through the stage of dehydrogenation into alkenes are expounded in the preceding paper [1]. In the case of alkenes, however, the double bond, though it can move to some extent along the carbon chain, is nevertheless to a considerable extent fixed. This is particularly true of hydrocarbons that already have a methyl side group. This probably explains the great ease of formation of dimethylalkanes, because the formation of a reaction center in the molecule of a branched paraffin has almost the same probability as in the molecule of a normal paraffin. It is understandable that in the case of the isomerization of alkenes the reaction center is limited to a small number of carbon atoms close to the double bond.

In conclusion we must point out that the products of the isomerization of the highest-boiling alkanes included some aromatic hydrocarbons (7-10%), formed as a result of the low pressure of hydrogen in these experiments. Complete inhibition of their formation can be effected only by increase in pressure (to about 20-25 atm), and this, in its turn, is associated with the selection of special catalysts permitting operations at any pressure with hydrocarbons boiling up to 300°.

SUMMARY

1. A study was made of the isomerization of various paraffins having 12-16 carbon atoms in presence of a multifunctional catalyst and of hydrogen under pressure.
2. In the isomerization of paraffins of a given molecular weight, branched paraffins, predominantly dimethylalkanes, are formed.
3. A catalyst was found which has reduced cleavage power under the conditions for the isomerization of high-boiling hydrocarbons.
4. A thermodynamic calculation was made of the "realizable-equilibrium composition" for C_{12} - C_{16} paraffins.

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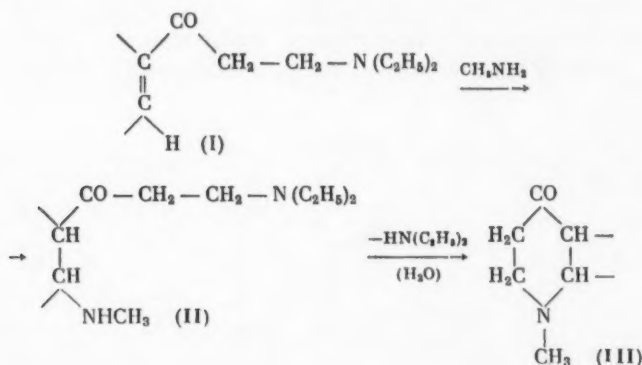
ACETYLENE DERIVATIVES

COMMUNICATION 183. NEW METHOD FOR THE SYNTHESIS OF 4-PIPERIDONES: ACTION OF AMMONIA OR PRIMARY AMINES ON 1-ALKENYL 2-DIALKYLAMINOETHYL KETONES

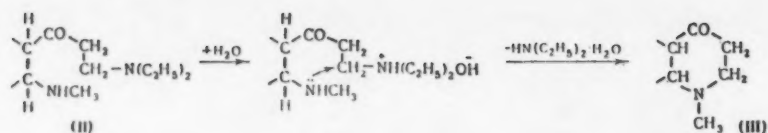
I. N. Nazarov and E. A. Mistrjukov

In the preceding communication [1] we described the synthesis of 4-piperidones by the cyclization of divinyl ketones prepared by the cleavage of methiodides of 1-alkenyl 2-diethylaminoethyl ketones [2]. However, it was later shown that these same 4-piperidones are much more conveniently prepared directly from unsaturated β -amino ketones, with omission of the stage of the conversion of the latter into divinyl ketones. The present communication is devoted to this question.

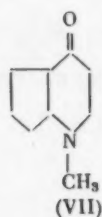
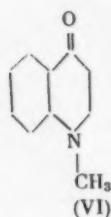
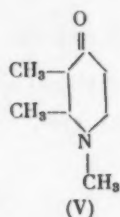
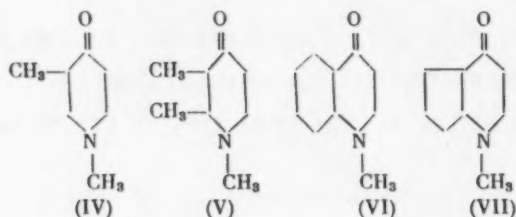
When aqueous methylamine is mixed with a 1-alkenyl 2-diethylaminoethyl ketone, the amino ketone is rapidly dissolved with appreciable evolution of heat. When the resulting solution is heated, diethylamine is liberated smoothly and the 4-piperidone is formed in up to 95 % yield. The cyclization of unsaturated β -amino ketones (I) into 4-piperidones (III) passes through the formation of diamino ketones (II) by addition of methylamine at the double bond in accordance with the following scheme:



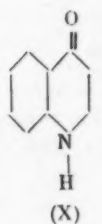
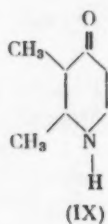
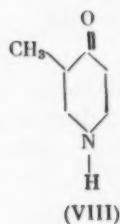
The β,β' -diamino ketones (II) formed in this way lose diethylamine quantitatively when heated and give 4-piperidones. It must be pointed out that the cyclization of β,β' -diamino ketones (II) into 4-piperidones (III) proceeds only in presence of water. Thus when the addition of methylamine to the unsaturated amino ketone (I) is carried out in an anhydrous medium, e.g. methanol, and the methanol and excess of methylamine are then removed under reduced pressure, the oily residue (the diamino ketone (II)) gives only traces of piperidone fraction, even when it is heated considerably beyond the boiling point of the piperidone (with further heating complete resinification of the diaminoketone (II) occurs). When, however, this residue is heated with water, diethylamine is eliminated almost quantitatively and the 4-piperidone is formed in a yield of over 90 %. Water, evidently, is necessary for the ammonization of the diethylamino group in the diamino ketone (II) and also for the reduction in the energy of elimination of diethylamine owing to the hydration of the latter.



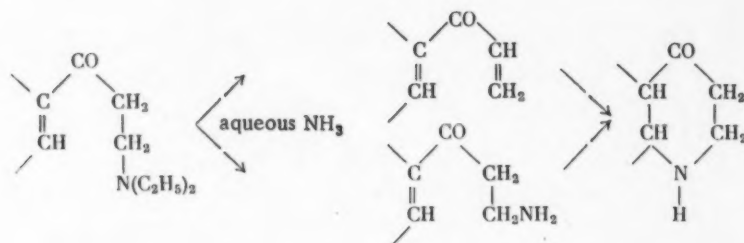
In this way, by the action of aqueous methylamine on the previously described [2] 1-alkenyl 2-diethylaminoethyl ketones (I) with subsequent heating of the solution to 80-95°, we prepared the 4-piperidones (IV)-(VII), which are of interest to us in connection with the search for new highly active anesthetics:



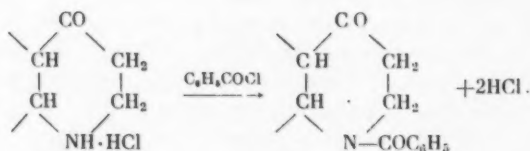
In a similar way, by the action of aqueous ammonia on 1-alkenyl 2-diethylaminoethyl ketones (I) we prepared the piperidones (VIII)-(XI), which do not contain a substituent on the nitrogen, in about 60% yield:



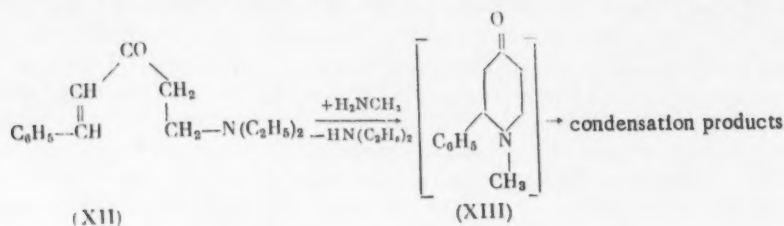
This process requires more severe conditions than in the case of methylamine and proceeds possibly through the intermediate formation of a divinyl ketone or through preliminary amino-exchange and subsequent cyclization. In this case we did not succeed in isolating the corresponding diamino ketones of type (II).



The benzoyl derivatives of (IX) and (X) were prepared by heating the hydrochlorides of these piperidones with benzoyl chloride:



We tried also to apply the above-described method in the preparation of 1-methyl-2-phenyl-4-piperidone (XIII). However, when the unsaturated amino ketone (XII) [3] was heated with methylamine, although diethylamine was liberated, only nondistilling condensation products of the piperidone (XIII) were obtained:



EXPERIMENTAL

1,2,3-Trimethyl-4-piperidone (V). A mixture of 41.8 g (0.228 mole) of 1-diethylamino-4-methyl-4-hexen-3-one [2] and 24 ml (0.274 mole, i.e. 20% excess) of 36% aqueous methylamine was shaken for 10-15 minutes. The amino ketone dissolved completely with appreciable evolution of heat rise in temperature to about 40°. The resulting solution was heated at 90-93° (steady boil) in a feeble stream of nitrogen for one hour. The diethylamine that collected in the receiver was purified from methylamine impurity and water by boiling it over sodium hydroxide. The yield of diethylamine was 15 g (90%). The reaction mixture was cooled and saturated with potassium carbonate; the base was extracted with ether, dried, and distilled. The product, amounting to 30.64 g (95%), was 1,2,3-trimethyl-4-piperidone (V); b.p. 68-70° (7 mm); n_D^{25} 1.4690. It was purified from imine impurity by heating it with dilute hydrochloric acid, and it then had b.p. 63-64° (2.5 mm) and n_D^{20} 1.4678. Its picrate melted at 172° (from alcohol) and showed no depression with the sample described previously [1].

Octahydro-1-methyl-4(1H)-quinolone (VI). A mixture of 32 g (0.155 mole) of 1-cyclohexen-1-yl 2-diethylaminoethyl ketone [2] and 18.5 ml (0.233 mole, i.e. 50% excess) of 36% aqueous methylamine was shaken in an open vessel at 30-35° until the amino ketone dissolved completely (90 minutes). The resulting solution was heated as in the preceding experiment at 90-95° for 50 minutes. The base was liberated from solution by saturation with potassium carbonate and was extracted with ether. Distillation gave 24.4 g (94% of octahydro-1-methyl-4-(1H)-quinolone (VI); b.p. 71-72.5° (0.5 mm); n_D^{20} 1.4962. After purification from imine as described previously, the substance had b.p. 67-68° (0.1 mm); n_D^{25} 1.4958.

Found %: C 72.05; H 10.37; N 8.60 $\text{C}_{10}\text{H}_{17}\text{NO}$. Calculated %: C 71.9; H 10.2; N 8.38.

Its picrate had m.p. 193-194° (from a mixture of dioxane and isobutyl alcohol).

Hexahydro-1-methyl-5H-1-pyridin-4(1H)-one (VII). Unpurified 1-cyclopenten-1-yl 2-diethylaminoethyl ketone, prepared by the hydration of 185 g of 3-(1-cyclopenten-1-yl)-N,N-diethyl-2-propynylamine [2], was added with stirring and cooling (temperature not above 25°) to 105 ml of 40% aqueous methylamine. The resulting solution was stirred for 30 minutes and then heated at 80-92° in a feeble stream of nitrogen for one hour. The diethylamine liberated was collected and purified as described above; yield 93 ml. The reaction product was isolated as in the preceding experiment. The product, amounting to 109.4 g (68% on the original enynylamine), was hexahydro-1-methyl-5H-1-pyridin-4-(1H)-one (VII), b.p. 80-83° (2 mm). After purification from imine as described previously, the substance had b.p. 62-63° (0.5 mm); n_D^{25} 1.4957; it was a colorless liquid of feeble odor; it darkened rapidly in the air.

Found %: C 70.87; H 9.93; N 9.31 $\text{C}_9\text{H}_{15}\text{NO}$. Calculated %: C 70.7; H 9.80; N 9.17.

Its picrate melted with decomposition at 170-171° (from aqueous alcohol).

1,3-Dimethyl-4-piperidone (IV). 5-Diethylamino-2-methyl-1-penten-3-one [2] (18.8 g, i.e. 0.111 mole) was added under ice-cooling to 18 ml (0.222 mole) of 40% aqueous methylamine and the resulting solution was heated at 80-85° for 30 minutes in a feeble stream of nitrogen. The piperidone formed was isolated from the reaction mixture as described above. The product, amounting to 8.5 g (60%), was 1,3-dimethyl-4-piperidone; b.p. 35-36° (1.5 mm); n_D^{20} 1.4620. Its picrate melted at 191-192°, alone and in admixture with a sample prepared in a different way [4].

Reaction between 1-Diethylamino-4-methyl-4-hexen-3-one and Methylamine in an Anhydrous Medium.

A mixture of 34.4 g (0.187 mole) of 1-diethylamino-4-methyl-4-hexen-3-one [2] and 45 ml (0.374 mole) of a 26% methanolic solution of methylamine was prepared, and the resulting solution was left for one hour at room temperature. Methanol and excess of methylamine were then distilled off under reduced pressure by heating the mixture to 35°; when the residue was heated to 100° at a residual pressure of 7 mm, only 6 g of distillate was collected. The oily residue, which consisted of the diamino ketone (II), was heated with 20 ml of water for 20 minutes at 80-90°, and the diethylamine liberated was collected and purified as indicated above. The yield of diethylamine was 11.0 g (80%). The reaction mixture was then saturated with potassium carbonate and extracted with ether; the ether extract was dried with potassium carbonate, ether was removed, and the residue was distilled at a residual pressure of 7 mm until the temperature reached 100°. A further amount (about 16 g) of distillate was collected (21.5 g in all). Redistillation gave 19.49 g of 1,2,3-trimethyl-4-piperidone, b.p. 67-69°, the picrate of which showed no depression of melting point with the sample prepared previously. When the addition of methylamine to the 1-alkenyl 2-diethylaminoethyl ketone is carried out in an aqueous medium and the resulting solution of the diamino ketone (II) is not heated as in the above-described experiments, but is carefully saturated with potassium carbonate under cooling and extracted with ether then in the distillation of the dried ether extract a similar picture is observed: only a very small amount of piperidone distills off. The bulk of the piperidone can be distilled off only after the nondistilling residue is heated with water.

2,3-Dimethyl-4-piperidone (IX). A mixture of 15.8 g (0.087 mole) of 1-diethylamino-4-methyl-4-hexen-3-one [2], 10 ml of 25% aqueous ammonia, and 10 ml of dioxane was heated in a metal ampoule at 95-100° for two hours. The reaction mixture was then transferred to a distillation flask, and at 100° in a feeble stream of nitrogen, diethylamine was distilled off for 45 minutes. The base was isolated in the usual way. The product, amounting to 7.17 g (65%), was 2,3-dimethyl-4-piperidone (IX); b.p. 63-66.5° (4 mm); $n_D^{22.5}$ 1.4710. The base was dissolved in alcohol and treated with the equivalent amount of alcoholic hydrogen chloride. The precipitated hydrochloride of 2,3-dimethyl-4-piperidone melted at 185.5-186° (from a mixture of alcohol and ethyl acetate).

Found %: C 51.39; H 8.65; N 8.52; Cl 21.56 $C_7H_{14}NOCl$. Calculated %: C 51.3; H 8.56; N 8.56; Cl 21.7.

Octahydro-4-(1H)-quinolone (X). A mixture of 18.7 g (0.089 mole) of 1-cyclohexen-1-yl 2-diethylaminoethyl ketone [2], 10.2 ml (0.133 mole) of 24% aqueous ammonia, and 9 ml of dioxane was heated as in the preceding experiment. The product, amounting to 9.0 g (66%), was octahydro-4 (1H)-quinolone (X); b.p. 80-83° (1 mm); n_D^{20} 1.5042. The base was dissolved in 15 ml of ethyl acetate and treated with 14 ml of a 4.16 N solution of hydrochloride in dioxane. The resulting hydrochloride of octahydro-4 (1H)-quinolone (yield 8.7 g) was recrystallized from alcohol and then melted with decomposition at 220.5-221.5° (in a sealed capillary).

Found %: C 57.2; H 8.56; Cl 18.55 $C_9H_{16}NCl$. Calculated %: C 57.2; H 8.46; Cl 18.7.

Hexahydro-5H-1-pyridin-4-(1H)-one (XI). A mixture of 18 g (0.092 mole) of unpurified 1-cyclopenten-1-yl 2-diethylaminoethyl ketone [2], 10.6 ml (0.138 mole) of 13 N aqueous ammonia, and 9 ml of dioxane was heated at 100° for 90 minutes as described above; it was treated in the usual way. The product, amounting to 5.9 g (46%), was hexahydro-5H-1-pyridin-4-(1H)-one (XI); b.p. 73-75° (1 mm); n_D^{19} 1.50703; the hydrochloride, prepared as in the preceding experiment, melted at 132-133° (from a mixture of ethyl acetate and alcohol).

Found %: C 54.30; H 7.99; N 7.63; Cl 20.03 $C_6H_{14}NOCl$. Calculated %: C 54.7; H 7.98; N 7.37; Cl 20.2.

3-Methyl-4-piperidone (VIII). A mixture of 38 g of liquid ammonia and 19.2 g of 5-diethylamino-2-methyl-1-penten-3-one [2] was prepared, and the resulting solution was left in an open vessel at room temperature for two days. Ammonia was then evaporated off, and the residue was heated with 30 ml of water at 90-95° for one hour. Only a small amount of diethylamine distilled off. The reaction mixture was saturated with potassium carbonate and extracted with ether. Distillation of the ether extract gave 1.35 g of 3-methyl-4-piperidone (VIII); b.p. 50-51° (2 mm) n_D^{19} 1.4744. Its hydrochloride had m.p. 176.5-177° (from alcohol).

Found %: C 48.18; H 8.05; N 9.65 $C_6H_{12}NOCl$. Calculated %: C 48.2; H 8.05; N 9.37.

Its picrate had m.p. 91-92° (from alcohol).

1-Benzoyloctahydro-4-(1H)-quinolone. A mixture of 3.97 g of the hydrochloride of octahydro-4 (1H)-quinolone, 3 ml of benzoyl chloride, and 10 ml of dichloroethane was boiled until hydrogen chloride ceased

to be evolved (20 hours). Solvent was then removed under reduced pressure, and the residue was crystallized from a mixture of benzene and isooctane. The product (5.15 g) was 1-benzoyloctahydro-4(1H)-quinolone, m.p. 105-106°.

Found %: C 74.96; H 7.43; N 5.64; $C_{18}H_{19}NO_2$. Calculated %: C 74.7; H 7.38; N 5.45.

1-Benzoyl-2,3-dimethyl-4-piperidone. A mixture of 1 g of the hydrochloride of 2,3-dimethyl-4-piperidone, 0.79 ml of benzoyl chloride, and 2.5 ml of dichloroethane was boiled until hydrogen chloride ceased to be evolved (9 hours). The reaction mixture was treated as in the preceding experiment, but only a very small amount of a crystalline isomer of 1-benzoyl-2,3-dimethyl-4-piperidone, m.p. 72-73° (from isooctane), was obtained.

Found %: C 78.14; H 7.42; N 5.94. $C_{14}H_{17}NO_2$. Calculated %: C 72.80; H 7.37; N 6.07.

SUMMARY

A new simple method was developed for the synthesis of 4-piperidones by the action of ammonia or primary amines on 1-alkenyl 2-diethylaminoethyl ketones, which are readily obtained from hydrocarbons derived from 1-buten-3-yne.

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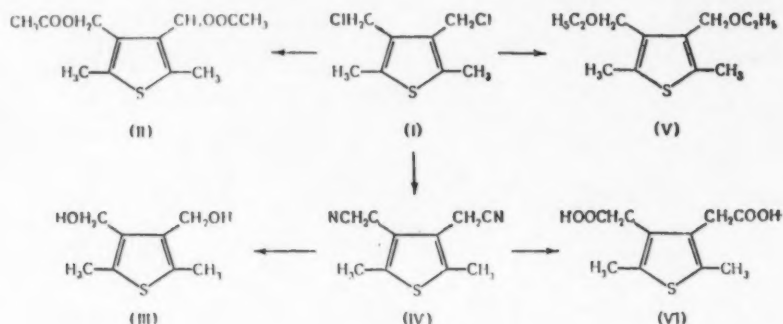
SYNTHESIS OF BIFUNCTIONAL COMPOUNDS FROM 2,5-DIMETHYLTHIOPHENE

M. S. Kondakova and Ia. L. Gol'dfarb

The sulfur compounds formed in the thermal decomposition of Kashpir shales include 2,5-dimethylthiophene, which is present in fairly large amount [1]. It was desirable to study ways of using this compound in the preparation of simple bifunctional compounds that might be of interest for further syntheses in the fields of high polymers and physiologically active substances. As starting material in the synthesis of bifunctional compounds from 2,5-dimethylthiophene we used 3,4-bis(chloromethyl)-2,5-dimethylthiophene (I), some reactions of which we have described in a previous paper [2].

By the action of sodium acetate on (I) under conditions similar to those used in the analogous reaction of 2,5-bis(chloromethyl)thiophene [3] we obtained an 80% yield of 2,5-dimethyl-3,4-thiophenedimethanol diacetate (II), which was converted by alcoholic sodium ethoxide into the corresponding diol 2,5-dimethyl-3,4-thiophenedimethanol (III). The readiness with which the chlorines of (I) are replaced under the action of nucleophilic reagents is exhibited also in its reactions with alcohol and potassium cyanide. When (I) was heated with the latter in aqueous acetone, it gave the corresponding dinitrile, i.e. 2,5-dimethyl-3,4-thiophenediacetonitrile (IV), but in this case the yield did not exceed 33%. It is probable that in presence of water the replacement of chlorine by the nitrile group is accompanied by hydrolysis to the diol with consequent reduction in the yield of nitrile. We did not succeed in improving the yield of (IV) by replacing aqueous acetone by aqueous dioxane and by raising the temperature: when this was done most of the product resinified.

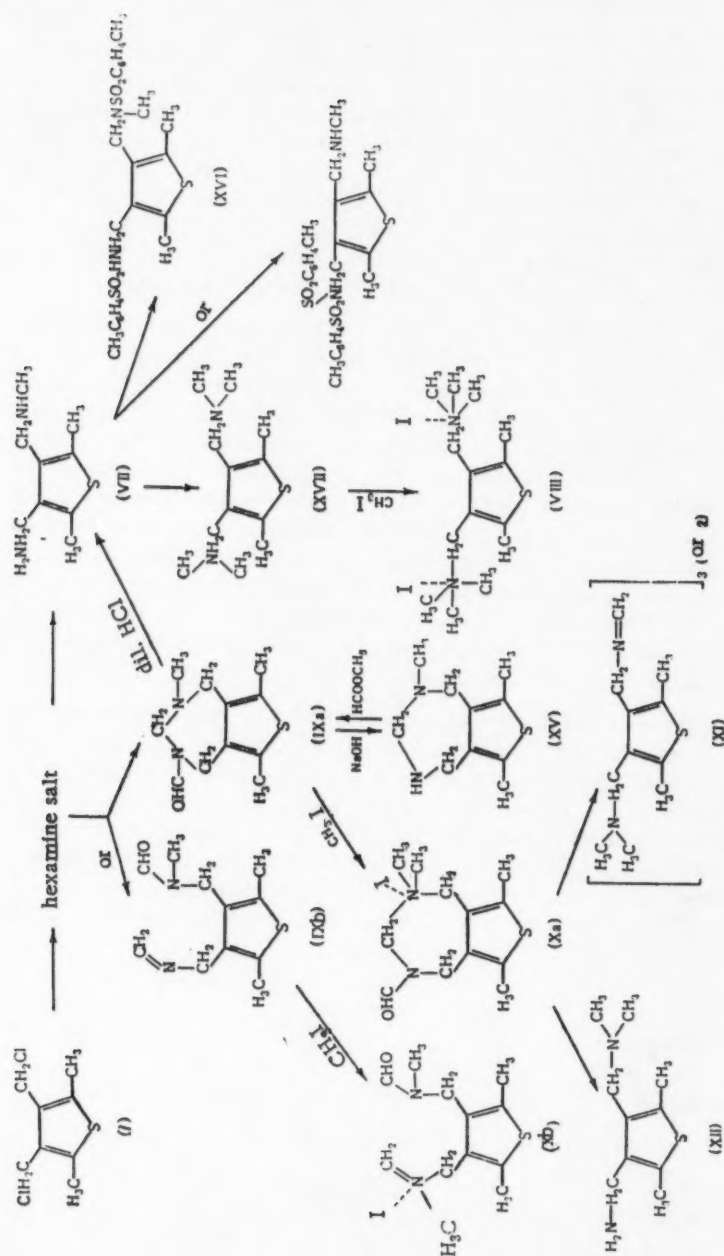
On analogy with the conditions used in the preparation of the nitrile from benzyl chloride it might be suggested that aqueous alcohol might be used as medium, but under such conditions the formation of nitrile can be accompanied by the formation of the ether. The latter, i.e.



Scheme 1

3,4-bisethoxymethyl-2,5-dimethylthiophene (V) was indeed formed when (I) was heated in a water bath with aqueous ethanol. A similar phenomenon was observed previously by Cairns and McKusick [4] in the reaction with 2-thenyl chloride. By the alkaline hydrolysis of the dinitrile (IV) under the conditions described by Ford et al. [5] for 2-thiopheneacetonitrile we obtained a small yield of 2,5-dimethyl-3,4-thiophenediacetic acid (VI) (Scheme 1).

Whereas these reactions led us directly to the expected compounds so that there remains only the task of

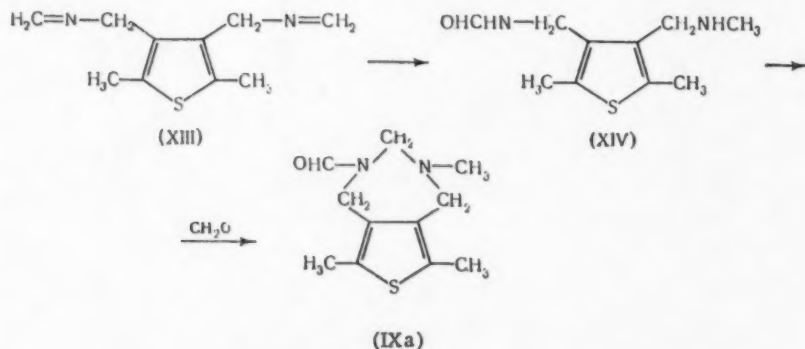


Scheme 2

finding the conditions for increased yields of these compounds, in experiments on the preparation of a diamine from (I) we met several complications. For this preparation we selected the very convenient method of Delepine [6, 7], i.e. the hydrolysis in an acid medium of the salt formed by (I) with hexamethylenetetramine (the "hexamine salt"), but instead of a symmetrical amine we obtained an unsymmetrical one corresponding in composition to (VII). This base was converted into a bis-*p*-tolylsulfonyl derivative by the action of *p*-toluene sulfonyl chloride, and this underwent methylation in an alkaline medium and therefore contained active hydrogens. These properties are in accord with the structure (VII) for the diamine, which contains three replaceable hydrogens; the composition of (VIII), the product of the exhaustive methylation of the diamine, also supports this view of the structure of the diamine. Since we started from the symmetrical dihalo compound (I), it seemed to be quite probable that the formation of the unsymmetrical amine (VII) was preceded by that of an intermediate compound, from which (VII) itself was formed. This compound, m.p. 132°, was isolated by treatment of the hexamine salt with steam. Under such conditions such salts generally yield aldehydes; in the present case this did not occur, probably because of the occurrence of the ortho effect [8]. On the basis of the composition and character of the starting compounds, the compound of m.p. 132° can be assigned the structure (IXa) or (IXb). The results of our investigation of this compound do not permit us to make a final choice between these two formulas, but it may be considered that formula (IXa) is the more probable.

When the substance of m.p. 132° was heated with dilute hydrochloric acid, it underwent a profound change with formation of the above-described base (VII), which can be prepared directly from the hexamine salt of (I). In an alkaline medium the hydrolysis can be stopped at the stage of the elimination of the formyl group, and it is then possible to isolate a certain amount of the base (XV) $C_{10}H_{16}N_2S$, which on treatment with methyl formate under the conditions described by Traube again gives the formyl derivative (IXa) or (IXb). This last compound can be isolated also from the mixture formed when the diamine (VII) is heated with a mixture of formalin and formic acid. With excess of methyl iodide (IX) (a or b) gives a monomethiodide. All these properties are in keeping with both formulas (IXa) and (IXb). However, the results of an investigation of the methiodide formed by this base can be given a simple explanation only if we assume the structure (Xa) and not (Xb). The fact that this salt can be recrystallized from water or alcohol is already evidence against the formula (Xb). As shown by Decker and Becker [10] and later by Graymore [7], alkyl halides of azomethines are very readily broken down, often in the cold, by the action of water or alcohol with formation of secondary amines and, in the case of methyleneamines, formaldehyde.

However, even the changes occurring when caustic alkali solution reacts with this methiodide are not associated with change in the number of carbon atoms in the molecule; the compound formed can be vacuum-distilled, and it undergoes rapid spontaneous polymerization. Molecular-weight determinations do not enable us to decide whether it is a trimer or dimer of the methyleneamine (see (XI), Scheme 2). In this connection it should be noted that other methyleneamines of this type, e.g. *N*-methylenebenzylamine, exist in the form of the trimer [11]. In an acid medium (XI) is hydrolyzed to a diamine, the structure of which is expressed by the formula (XII), if we assume that the formyl derivative and the methiodide have the structures (IXa) and (Xa) respectively. The relationships between the various compounds characterized are shown in Scheme 2.



Turning to the question of the mechanism of the formation of (IXa), we must first point out that it is difficult to be sure of the sequence of the changes occurring. One possibility is that the symmetrical azomethine (XIII) first formed [12] or the corresponding bishydroxymethyl compound undergoes an intramolecular reaction with formation of the formyl derivative (XIV). Such a reaction, which, like the Cannizzaro reaction, is an oxidation-reduction process, occurs (according to Decker and Becker's views) in the methylation of ammonia by Plochl's method [13].

The next stage of the process consists in the condensation of formaldehyde, formed in the hydrolysis of the hexamine salt, with N-formyl-N', 2,5-trimethyl-3,4-thiophenebismethylamine (XIV). Such condensations of acid amides proceed, as Einhorn showed [14], under very mild conditions.

EXPERIMENTAL

2,5-Dimethyl-3,4-Thiophenedimethanol Diacetate (II)

A mixture of 10.6 g of anhydrous sodium acetate, 42 ml of glacial acetic acid, and 12.6 g of 3,4-bis-chloromethyl-2,5-dimethylthiophene was heated for six hours in a water bath at 60°, after which it was left at room temperature until the next day. The precipitate of inorganic salts that separated was filtered off and washed with acetic acid. Acetic acid was distilled from the filtrate under reduced pressure. Water was added to the oily residue, which then crystallized. The crystals were filtered off and washed with water. The yield of impure product was 12.5 g (81%); the melting point after repeated crystallization from alcohol was 57-58°.

Found %: C 56.32; 56.47; H 6.36; 6.23; S 12.64; 12.86. $C_{12}H_{16}O_4S$. Calculated %: C 56.25 H 6.25 S 12.50.

2,5-Dimethyl-3,4-Thiophenedimethanol (III)

2,5-Dimethyl-3,4-thiophenedimethanol diacetate (8.7 g) was added to a solution of 0.2 g of sodium in 60 ml of absolute alcohol; the mixture was kept at room temperature for 60 hours. The solution was evaporated to small bulk, 5 g of ammonium chloride was added, and the inorganic salts were then filtered off and washed with absolute alcohol. Alcohol was distilled from the filtrate. The residue (6.5 g) melted at 62-70°. After repeated crystallizations from heptane the substance melted at 76-77°.

Found %: C 55.93; 55.84; H 6.97; 6.88; S 18.50; 18.58. $C_8H_{12}O_2S$. Calculated %: C 55.81; H 6.97; S 18.60.

2,5-Dimethyl-3,4-Thiophenediacetonitrile (IV)

A mixture of 3.3 g of potassium cyanide, 4.5 ml of acetone, 4.5 ml of water, and 5 g of 3,4-bis-chloromethyl-2,5-dimethylthiophene was heated at 80-90° in a water bath for four hours. When cool, the mixture was diluted with water and extracted with benzene; the benzene was distilled off under reduced pressure. The residue was transferred to a funnel and washed with ether. We obtained 1.5 g (33%) of crystalline substance, m.p. 123-125°. Recrystallization from heptane gave 2,5-dimethyl-3,4-thiophenediacetonitrile, m.p. 125-125.5°.

Found %: C 63.27; 63.31; H 5.21; 5.21; S 16.86; 16.98; N 14.75. $C_{10}H_{10}N_2S$. Calculated: %: C 63.15; H 5.26; S 16.84; N 14.74.

3,4-Bisethoxymethyl-2,5-Dimethylthiophene (V)

Water (100 ml) was added to a solution of 4 g of 3,4-bis-chloromethyl-2,5-dimethylthiophene in 100 ml of ethanol, and the mixture was heated in a water bath for four hours. Alcohol and part of the water were then distilled off under reduced pressure. The oil that separated was extracted with benzene. The benzene solution was dried over anhydrous $MgSO_4$, benzene was distilled off, and the residue was vacuum-distilled. The product (2.5 g) had b.p. 155-161° (20 mm).

Found %: C 62.95; 62.98; H 8.68; 8.81; S 14.33. $C_{12}H_{20}O_2S$. Calculated %: C 63.15; H 8.76; S 14.03.

2,5-Dimethyl-3,4-Thiophenediacetic Acid (VI)

A mixture of 1.3 g of 2,5-dimethyl-3,4-thiophenediacetonitrile, 1.5 g of KOH, 7.5 ml of water, and 7.5 ml

of alcohol was heated in a water bath for 12 hours. Alcohol was distilled off under reduced pressure, and water and hydrochloric acid were added to the residue. The undissolved substance was filtered off, washed with ether, and crystallized from aqueous alcohol. We obtained 0.5 g of an acid, sparingly soluble in ether and benzene, m.p. 182-183°.

Found %: C 53.07; 53.05; H 5.35; 5.36 $C_{10}H_{12}O_4S$. Calculated %: C 52.63; H 5.26.

N, 2, 5-Trimethyl-3, 4-Thiophenebismethylamine (VII)

The quaternary salt (18 g) obtained from 7.5 g of 3,4-bischloromethyl-2,5-dimethylthiophene and 11 g of hexamethylenetetramine was mixed with 75 ml of ethanol and 25 ml of concentrated hydrochloric acid. The mixture was heated in a water bath for four hours. The salt went into solution, and then a crystalline precipitate A was formed. This was filtered off, and alcohol was distilled from the filtrate. A mixture of the residue and A was dissolved in water in a water bath. The solution was cooled, and 40% KOH solution was added. The oil that separated was extracted with ether, the ether extract was dried over $MgSO_4$, and ether was distilled off, leaving an oily residue. Vacuum distillation of the residue at 20 mm residual pressure gave 2.8 g of a colorless substance, b.p. 158-164°. In another experiment, 85 g of the quaternary salt gave 16.1 g of base, b.p. 127° (8 mm); yield 50%.

Found %: C 58.22; 58.23; H 8.71; 8.76; S 17.45; 17.70; N 15.36 $C_9H_{16}N_2S$. Calculated %: C 58.69; H 8.70; S 17.39; N 15.21.

Hydrochloride. The hydrochloride of the base was prepared by the action of alcoholic HCl. After repeated crystallization from alcohol it melted with decomposition at 265-268°.

Found %: N 11.00; 10.70 $C_9H_{16}N_2S \cdot 2HCl$. Calculated %: N 10.89.

Picrate. The picrate was prepared by mixing alcoholic solutions of the base and picric acid. After being crystallized from alcohol the picrate had m.p. 182-183°. (with decomposition).

Found %: C 39.48; 39.23; H 3.72; 3.75; S 4.88; 4.84; N 17.27; 17.23 $C_9H_{16}N_2S \cdot 2C_6H_2(NO_2)_3OH$. Calculated %: C 39.25; H 3.42; S 4.98 N 17.44.

Bis-p-tolylsulfonyl Derivative (XVI)

A solution of 5.7 g of p-toluenesulfonyl chloride in 30 ml of ether was added in small portions with shaking and cooling with ice water to a mixture of 2.7 g of the base (VII) in 10 ml of ether and 3 g of NaOH in 37 ml of water. The mixture was then shaken for ten hours. The reaction product was filtered off (6.6 g) and crystallized from alcohol. The product (5 g) was the compound (XVI), m.p. 142-145°; found M 478; calculated M 492.

Found %: C 56.08; 56.20; H 5.83; 5.80; S 19.54; 19.00; N 6.13; 6.23 $C_{23}H_{28}N_2O_4S_2$. Calculated %: C 56.09; H 5.69; S 19.51; N 5.69.

Methyl iodide (3 g) was added to a mixture of 1 g of the p-tolylsulfonyl derivative of m.p. 142-145° and a solution of 0.1 g of sodium in 30 ml of alcohol. The mixture was heated in a water bath (60-65°) for 25 minutes; the substance then went into solution; the solution was then saturated with carbon dioxide. The precipitate that formed was filtered off and washed with alcohol. The methylation product (0.8 g) had m.p. 153-154°. After recrystallization from alcohol it had m.p. 153-154.5°.

Found %: C 56.72; 56.79; H 6.01; 6.01; S 18.97; 19.00; N 5.62; 5.56 $C_{24}H_{30}N_2O_4S_2$. Calculated %: C 56.91; H 5.93; S 18.97; N 5.53.

2, 3, 4, 5-Tetrahydro-4, 6, 8-Trimethyl-1H-Thieno [3, 4-e] [1, 3] Diazepine-2-Carboxaldehyde (IXa)

A solution of 20 g of the quaternary salt prepared from 3,4-bischloromethyl-2,5-dimethylthiophene and hexamethylenetetramine in 50 ml of hot water was subjected to treatment with steam. A very small amount of oily material passed over into the distillate. Hydrochloric acid was added to the cooled residue in the distillation flask, and the mixture was extracted with ether. This extract contained only traces of substance and was not investigated further. To the aqueous layer 40% NaOH solution was added. The oil that was liberated was extracted with ether. Solvent was distilled from the resulting solution, and the residue (1.3 g) was crystallized from heptane. After being recrystallized from heptane, the product (IXa) had m.p. 132-132.5°.

Found %: C 59.31; 59.11; H 7.32; 7.26; S 14.21; 14.34; N 12.26; 12.28; $C_{11}H_{16}N_2OS$. Calculated %: C 58.93; H 7.14; S 14.28; N 12.50.

The ether-insoluble part of the product was treated with hot benzene; solvent was distilled from the benzene solution; the residue (2.5 g) was a crystalline substance. After being crystallized from heptane the substance melted at 132-132.5° and was found to be identical with the substance isolated from the ether extract; found M 219, 226; calculated M 224. The base (IXa) does not contain active hydrogen.

In another experiment 59.7 g of the hexamine salt gave 17 g of 2,3,4,5-tetrahydro-4,6,8-trimethyl-1H-thieno [3,4-e] [1,3] diazepine-2-carboxaldehyde, which, after being crystallized from acetone, melted at 132-132.5°.

Hydrolysis of 2,3,4,5-Tetrahydro-4,6,8-Trimethyl-1H-Thieno [3,4-e] [1,3]-Diazepin-2-carboxaldehyde

A. A solution of 6.7 g of the base of m.p. 132° in 50 ml of 1 : 1 hydrochloric acid was heated to the boil in the course of 3.5 hours and was then evaporated to dryness under reduced pressure. The residue was dissolved in water, and 40% KOH was added to the solution. The dark-colored oil that separated was extracted with ether. The ether extract was dried over potassium carbonate, ether was distilled off, and vacuum distillation of the residue gave 4.5 g of the base (VII) as a colorless mobile oil, b.p. 138-141° (10 mm), which absorbed carbon dioxide from the air. The base was converted into its hydrochloride, which melted with decomposition at 263-264° after repeated crystallization from alcohol. A mixture with the hydrochloride of N,2,5-trimethyl-3,4-thiophenebismethylamine melted without depression.

Found %: C 41.95; 42.12; H 7.04; 7.17; N 11.01; 10.84 $C_9H_{16}N_2S \cdot 2HCl$. Calculated %: C 42.02; H 7.00; N 10.89.

B. A mixture of 5.5 g of the base (IXa), 80 ml of ethanol, and a solution of 2 g of NaOH in 10 ml of water was heated in a water bath for 18 hours. Alcohol was distilled off under reduced pressure, and water and 40% NaOH solution were added to the residue; an oil separated and was brought into solution by shaking with benzene. The alkaline aqueous solution was acidified to Congo red with sulfuric acid and was then steam-distilled. The distillate was titrated with 0.1 N NaOH. The result corresponded to 0.875 g of formic acid in the distillate, i.e. 77% of the amount calculated on the assumption that 1 molecular proportion of formic acid is formed under the conditions indicated above. Removal of solvent from the benzene extract gave 4.5 g of substance, and distillation of this at a residual pressure of 5 mm gave:

Fraction I, b.p. 125-128°; 2.2 g
Fraction II, b.p. 128-138°; 0.6 g
Fraction III, b.p. 138-158°; 0.4 g
Residue in flask 1.2 g

Fraction I was analyzed:

Found %: C 60.94; 61.09; H 8.21; 8.25; $C_{10}H_{16}N_2S$. Calculated %: C 61.23; H 8.16.

Hence, in composition this substance corresponded to a compound of structure (XV). Its picrate was prepared by mixing alcoholic solutions of the base and picric acid. After being recrystallized from alcohol with an addition of ether, the picrate melted with decomposition at 183°.

Found %: N 17.26; 17.10; $C_{10}H_{16}N_2S \cdot 2C_6H_2(NO_2)_3OH$. Calculated %: N 17.12.

Action of Methyl Formate on the Base (XV)

Methyl formate (0.7 g) was added to a solution of 1.07 g of the base in 3 ml of methanol, and the mixture was left overnight at room temperature. The mixture was then heated in a water bath for two hours, after which alcohol was distilled off. The residue was crystallized from heptane. The yield of product, m.p. 129-131°, was 0.4 g. A mixture with the base of m.p. 132° melted without depression.

Found %: C 58.80; 58.92; H 7.25; 7.16; N 12.12; 12.30 $C_{11}H_{16}N_2OS$. Calculated %: 55.93; H 7.14; N 12.50.

The methiodide (m.p. 216-219°) prepared from this base was found to be identical with the methiodide of the base (IXa).

The Methiodide (Xa) from the Base (IXa)

a) A mixture of 4.5 g of the base of m.p. 132°, 20 ml of absolute alcohol, and 15 g of methyl iodide was heated in a water bath for two hours and was then left at room temperature for three days. The precipitate formed was filtered off (7.3 g). After being crystallized from water and alcohol, the methiodide melted at 216-218°.

Found %: C 39.10; 39.32; H 5.43; 5.42; N 7.66; $C_{11}H_{16}N_2OS \cdot CH_3I$. Calculated %: C 39.34; H 5.19; N 7.65.

b) Methyl iodide (5 g) was added to a solution of 1 g of the base in 10 ml of benzene, and the mixture was heated in a water bath for two hours. The precipitate formed was filtered off. The melting point of the substance was 216-218°, but it gave no depression in admixture with the methiodide isolated in the experiment in an alcoholic medium (see above).

Hydrolysis of the Methiodide (Xa)

a) Formation of N,N,2,5-Tetramethyl-3,4-thiophenebismethylamine (XII). A solution of 3.6 g of the methiodide of m.p. 216-218° in 25 ml of 1:1 hydrochloric acid was heated to the boil in the course of two hours. The solution was cooled and shaken with ether. The ether layer was separated, and 40% KOH solution was added to the aqueous layer. The oil liberated was extracted, and the ether extract was dried over potassium carbonate. Ether was distilled off, and the residue (1.7 g) was distilled at a residual pressure of 6 mm. The base (N,N,2,5-tetramethyl-3,4-thiophenebismethylamine) is a colorless oil; in the air it absorbs carbon dioxide.

Found %: C 60.97; 60.37; H 9.26; 9.43; $C_{10}H_{18}N_2S$. Calculated %: C 60.60 H 9.09.

The hydrochloride of the base (XII) (m.p. 256-259°) showed no depression when melted in admixture with the hydrochloride isolated in the hydrolysis of the methiodide (Xa) in an alkaline medium (see below).

b) Formation of N,N,2,5-tetramethyl-N'-methylene-3,4-thiophenebismethylamine (XI). The methiodide (Xa) (5 g) was dissolved in hot water; the solution was cooled, and 8% NaOH solution was added until there was an alkaline reaction. The oil liberated was extracted with ether. The ether solution was separated and dried over potassium carbonate. Ether was distilled off and left a thick oily residue (3.3 g), which solidified on keeping. After being recrystallized from alcohol, the substance melted at 123-124°.

Found %: C 62.46; 62.54; H 8.54; 8.56; S 15.41; 15.43 $C_{11}H_{18}N_2S$. Calculated %: C 62.90; H 8.57; S 15.23.

Treatment of the substance of m.p. 124° with hydrochloric acid gave the hydrochloride, m.p. 256-258° (with decomposition).

Found %: C 44.56; H 7.43 $C_{10}H_{18}N_2S \cdot 2HCl$. Calculated %: C 44.28; H 7.38.

Action of Formaldehyde and Formic Acid on N,2,5-Trimethyl-3,4-thiophenebismethylamine

A mixture of 4.5 g of N,2,5-trimethyl-3,4-thiophenebismethylamine, 0.6 g of the paste obtained by evaporating 37% formalin, and 2.3 g of formic acid (96%) was heated in a water bath for two hours. Evolution of carbon dioxide was observed. When cool, the mixture was diluted with water, 40% NaOH solution was added, and the mixture was extracted with benzene. The benzene solution was washed with water, and benzene was distilled off under reduced pressure. Distillation of the residue at a residual pressure of 4 mm gave the following fractions:

Fraction I b.p. 110-145°; 1.3 g a liquid

Fraction II b.p. 145-163°; 0.9 g a solid

Fraction III b.p. 165-175°; 0.8 g a solid

Fraction II was crystallized from heptane; m.p. 132-132.5°.

Found %: C 58.86; 59.23; H 7.39; 7.18; S 14.23; 14.08; N 12.22 $C_{11}H_{16}N_2OS$. Calculated %: C 58.93; H 7.14; S 14.28; N 12.50.

In admixture with the base (IXa) (see above) there was no depression of melting point.

N,N,N',N',2,5-Hexamethyl-3,4-Thiophenebismethylamine (XVII)

N,2,5-Trimethyl-3,4-thiophenebismethylamine (5.5 g) was added with mechanical stirring to 15.4 g of methyl benzenesulfonate. During the mixing much heat was evolved and the mixture became dark-colored. The flask was cooled externally with water. When the evolution of heat ceased, the mixture was heated in an oil bath for 70 minutes at 155-165°. When cool, the mixture was dissolved in water and 40% KOH was added to the resulting solution. The oil liberated was extracted with ether. The ether extract was dried over potassium carbonate, and ether was distilled off. Dilute (1:1) hydrochloric acid was added to the residue, and the mixture was evaporated to dryness under reduced pressure. The dry residue was dissolved in hot methanol. Ether was added to the cool alcoholic solution until a turbidity was produced. The crystalline precipitate formed was filtered off. The colorless crystals (3.4 g) were repeatedly crystallized from methanol and then melted at 255-256° with decomposition.

Found %: C 45.34; 45.41; H 8.03; 7.78; $C_{12}H_{22}N_2S \cdot 2HCl \cdot H_2O$. Calculated %: C 45.42; H 8.20

The hydrochloride of m.p. 255-256° (3 g) was dissolved in water, and 40% KOH solution was added. The oil liberated was extracted with ether. The ether extract was dried over potassium carbonate, ether was distilled off, and the residue was vacuum-distilled: at 8 mm the base (1.5 g) boiled at 110°; it quickly solidified: m.p. 29.5-30.5°.

Found %: C 63.61; 63.46; H 9.67; 9.74; S 14.13; 13.97; $C_{12}H_{22}N_2S$. Calculated %: C 63.72; H 9.73; S 14.16.

N,N,N',N',2,5-Hexamethyl-3,4-Thiophenebismethylamine Dimethiodide (VIII)

Methyl iodide (4.4 g) was added to a solution of 1.5 g of the base of m.p. 29.5-30.5° in 50 ml of methanol and the mixture was heated in a water bath for four hours. The precipitate of methiodide was filtered off (2.7 g of crystals, which did not melt below 360°).

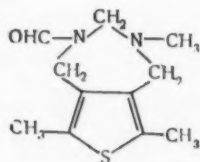
Found %: C 32.92; 32.94; H 5.68; 5.74 $C_{14}H_{28}I_2NS$. Calculated %: C 32.94; H 5.49.

SUMMARY

1. From 3,4-bis(chloromethyl)-2,4-dimethylthiophene, by the action of suitable reagents, the following were prepared: 2,5-dimethyl-3,4-thiophenedimethanol diacetate (II), 2,5-dimethyl-3,4-thiophenedimethanol (III), 2,5-dimethyl-3,4-thiophenediacetonitrile (IV), 3,4-bis(ethoxymethyl)-2,5-dimethylthiophene (V), and 2,5-dimethyl-3,4-thiophenediacetic acid (VI).

2. Hydrolysis of the hexamine salt formed by 3,4-bis(chloromethyl)-2,5-dimethylthiophene with hexamethylenetetramine gave not the symmetrical diamine, but N,2,5-trimethyl-3,4-thiophenebismethylamine.

3. An intermediate product formed in the course of the formation of the diamine has the composition $C_{11}H_{16}N_2OS$, and its structure is probably



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SYNTHESIS OF POLYALKYLENEARYLS

COMMUNICATION 5. EFFECT OF CATALYST CONCENTRATION ON
THE COURSE OF THE COPOLYCONDENSATION OF BENZENE AND
CHLOROBENZENE WITH 1,2-DICHLOROETHANE

G. S. Kolesnikov, V. V. Korshak, and A. P. Suprun

In the preceding communication we reported the results of a study of the effect of the temperature of reaction on the course of the copolycondensation of benzene and chlorobenzene with 1,2-dichloroethane [1]. Continuing this investigation, we have examined the effect of catalyst concentration on the course of the copolycondensation process. The experimental procedure was the same as that used previously [1]; the benzene: chlorobenzene molar ratio was 1 : 1, the aromatics : dichloroethane molar ratio was 1.5 : 1, and the reaction temperature was maintained at $65 \pm 0.02^\circ$. The concentration of aluminum chloride was varied from 1.5 to 12 moles per cent on the total aromatics. The results are given in Tables 1-4 and Figures 1 and 2.

It will be seen from Tables 1-4 and Fig. 1 that with increase in catalyst concentration the rate of the polycondensation of dichloroethane with a mixture of benzene and chlorobenzene rises; this is observed also in other polycondensation reactions [2, 3]. At an aluminum chloride concentration of 1.5 moles per cent polycondensation is extremely slow and the yield of copolymer after 90 minutes from the start of reaction is only 2.0%. Increase in the catalyst concentration to 3 moles per cent results in increased yield of copolymer, and after 90 minutes it attains 22.6%; further increase in catalyst concentration to 6 and 12 moles per cent results in increase in the yield of copolymer in the same interval of time to 49.0% and 74.3% respectively.

TABLE 1
Copolycondensation of Dichloroethane with Benzene and Chlorobenzene in Presence
of 1.5 Moles per Cent of Aluminum Chloride

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (mean) (%)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	Traces	—	—	—		
60	Traces	—	—	—		
90	2,0	1,97	16,0	106,1	Not determined because of small yield of copolymer	
150	4,5	2,27	14,7	106,3		
180	6,5	2,00	15,7	106,1		
210	8,5	2,71	11,2	106,9		

It must be pointed out that increase in the aluminum chloride concentration not only increases the rate of formation of the copolymer, but apparently favors also increased branching. Only by increased branching of the copolymer with increase in catalyst concentration can we explain the formation of a three-dimensional product after 120 minutes at an aluminum chloride concentration of 12 moles per cent. On the other hand, at lower catalyst concentrations the formation of a cross-linked structure is not observed even after more prolonged reaction.

TABLE 2

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene in Presence of 3.0 Moles per Cent of Aluminum Chloride

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (mean) (%)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	10,4	2,06	15,2	106,1	1950	18,4
60	18,8	2,21	14,1	106,3	2200	20,7
90	22,6	2,31	13,4	106,5	2380	22,3
120	27,9	2,66	11,5	106,8	2440	22,8
150	33,9	3,12	9,6	107,2	2550	23,8
180	38,7	3,43	8,6	107,6	2630	24,4
210	44,4	3,49	8,4	107,7	2840	26,6

TABLE 3

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene in Presence of 6.0 Moles per Cent of Aluminum Chloride

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (mean) (%)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	23,0	2,60	11,7	106,7	1970	18,5
60	39,1	3,83	7,6	108,0	2490	23,1
90	49,0	4,76	5,9	109,1	2650	24,3
120	60,3	4,86	5,7	109,2	2880	26,4
150	68,7	5,03	5,4	109,4	3040	27,8
180	76,8	5,32	5,1	109,7	3620	33,0
210	84,4	5,89	4,5	110,3	4010	36,4

TABLE 4

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene in Presence of 12 Moles per Cent of Aluminum Chloride

Duration of reaction (minutes)	Yield of copolymer (%)	Chlorine content of copolymer (mean) (%)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	52,5	4,50	6,2	108,7	2160	19,9
60	71,5	5,84	4,5	110,3	2750	24,9
90	74,3	7,70	3,1	112,4	4560	40,6
120	83,9	7,14	3,4	111,7	6670	59,7

Increase in the concentration of aluminum chloride results also in increase in the degree of polymerization of the copolymer formed (Fig. 2). Fig. 3 shows the variation of the degree of polymerization of the polycondensation product with yield. From Fig. 3 it will be seen that the degree of polymerization does not change greatly up to a yield of about 65%, and it is probable that up to this point the copolymer molecules are formed mainly by interaction between the growing copolymer molecules and molecules of the original reactants. However, as soon as the yield of copolymer begins to exceed 65-70%, the degree of polymerization rises sharply. As stated previously [1], this can be explained on the view that copolymer molecules take part in the polycondensation reaction as an aromatic component. It is to be expected that copolymer molecules can take part in chain growth only when their concentration is sufficiently high as to be comparable to that of the aromatic compounds of low molecular weight, which falls in the course of the reaction.

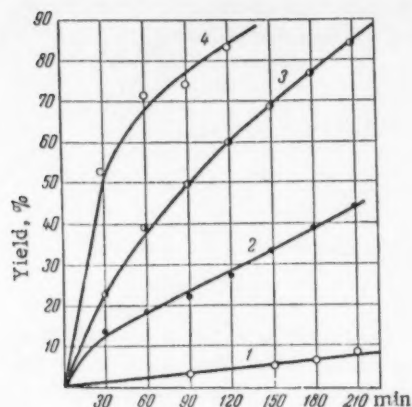


Fig. 1. Relation of yield of copolymer to duration of reaction: 1) 1.5 moles σ_6 ; 2) 3 moles σ_6 ; 3) 6 moles σ_6 ; 4) 12 moles σ_6 ; AlCl_3 .

increase in the duration of the reaction; the higher the concentration of aluminum chloride, the higher the chlorine content of the copolymer formed. This fact might form the basis for the hypothesis that the relative activity of chlorobenzene increases with increase in catalyst concentration. However, such a view is incorrect, because the increase in the chlorine content of the copolymer with increase in catalyst concentration is merely the result of the greater extent to which the original reactants are converted into copolymer. In fact, if we examine the change in the content of $-\text{C}_6\text{H}_4\text{ClCH}_2\text{CH}_2-$ fragments in the copolymer (Fig. 5), it is found that, irrespective of the catalyst concentration, the content of such fragments increases in proportion to the yield of copolymer or, in other words, to the degree of conversion of the original reactants into the macromolecular compound. Overberger also observed the absence of any effect of catalyst concentration on the relative activity of styrenes in their polymerization [4].

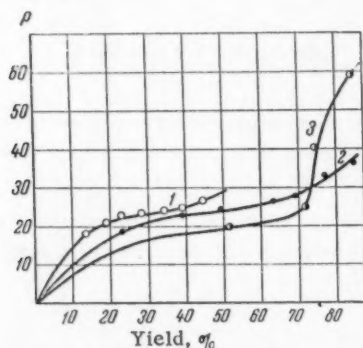


Fig. 3. Relation of degree of polymerization of copolymer to yield: 1) 3 moles σ_6 ; 2) 6 moles σ_6 ; 3) 12 moles σ_6 ; AlCl_3 .

Increase in the chlorine content of the copolymer as polycondensation proceeds indicates that benzene is more reactive than chlorobenzene; i.e. that benzene has the higher relative activity. During polycondensation the more active benzene is more rapidly exhausted and the chlorobenzene content of the reaction system increases. As a result, toward the end of the polycondensation process the extent to which the less active chlorobenzene takes part in the building of the copolymer

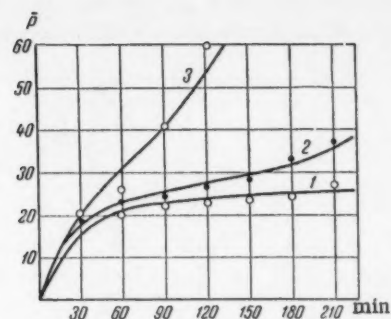


Fig. 2. Relation of degree of polymerization of copolymer to duration of reaction: 1) 3 moles σ_6 ; 2) 6 moles σ_6 ; 3) 12 moles σ_6 ; AlCl_3 .

As will be seen from Tables 1-4 and Fig. 4, the chlorine content of the copolymer increases with in-

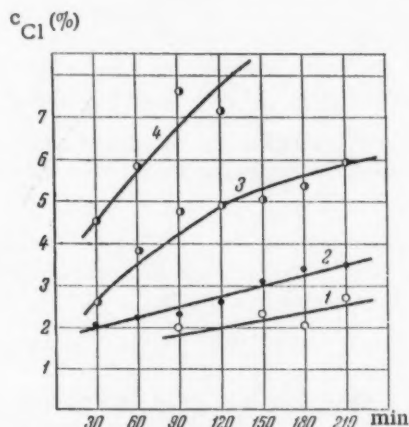


Fig. 4. Relation of chlorine content of copolymer to duration of reaction: 1) 1.5 moles σ_6 ; 2) 3 moles σ_6 ; 3) 6 moles σ_6 ; 4) 12 moles σ_6 ; AlCl_3 .

increases and the chlorine content of the copolymer increases. As will be seen from Tables 1-4, at all catalyst concentrations n/m is greater than unity; the relative activity of chlorobenzene in its reaction with dichloroethane in the system benzene-chlorobenzene-dichloroethane is therefore less than that of benzene.

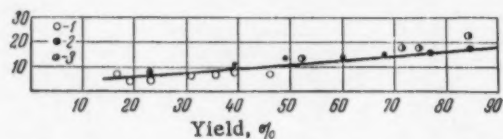


Fig. 5. Relation of the content of $-C_6H_3ClCH_2CH_2-$ fragments in the copolymer to the yield.

When the effects of temperature [1] and catalyst concentration on the polycondensation of dichloroethane with a mixture of benzene and chlorobenzene are compared it will be noted that these effects are in many ways analogous: both rise in temperature and increase in catalyst concentration lead to more rapid polycondensation, to an increase in the degree of polymerization, and finally to the formation of a cross-linked structure at yields of 80% and higher. However, there are some differences: the degree of polymerization at the point just before the formation of a cross-linked structure at 75° is 185.5, whereas at the point just before the formation of a three-dimensional polymer at an aluminum chloride concentration of 12 mole per cent it is only 59.7. This indicates that increase in the aluminum chloride concentration greatly increases the number of active centers at which the initiation of growing chains occur; this, in its turn, favors increase in the branching of the copolymer. Hence, increase in catalyst concentration favors increase in branching of the copolymer and formation of a cross-linked structure to a greater extent than rise in temperature (in the range studied).

It is characteristic also that with rise in reaction temperature the degree of polymerization of the copolymer formed in the first stage of the process increases only slightly, but when the yield of copolymer attains 50% there is an appreciable rise in degree of polymerization [1]. In the case of increase in the catalyst concentration (Fig. 3), the analogous increase in degree of polymerization occurs somewhat later (approximately on the attainment of a yield of 65%), i.e. the polymer molecules begin to participate in polycondensation as an aromatic component at a later stage of the process.

SUMMARY

1. The effect of aluminum chloride concentration on the course of the copolycondensation of 1,2-dichloroethane with benzene and chlorobenzene was studied.
2. With increase in the duration of reaction the chlorine content of the copolymer rises; this confirms the difference found previously in the relative activities of benzene and chlorobenzene in reaction with 1,2-dichloroethane.
3. A comparison was made between the effects of change of temperature of reaction and change of catalyst concentration on the course of the copolycondensation of 1,2-dichloroethane with benzene and chlorobenzene in presence of aluminum chloride.

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SYNTHESIS OF POLYALKYLENEARYLS

COMMUNICATION 6. EFFECT OF THE RELATIVE AMOUNTS OF
REACTANTS ON THE COURSE OF THE COPOLYCONDENSATION
OF BENZENE AND CHLOROBENZENE WITH 1,2-DICHLOROETHANE

G. S. Kolesnikov, V. V. Korshak, and A. P. Suprun

In previous communications we have examined the effects of temperature of reaction and catalyst concentration on the course of the copolycondensation of benzene and chlorobenzene with 1,2-dichloroethane in presence of aluminum chloride [1,2]. The present investigation had the object of determining the effect of the relative amounts of the reactants, and particularly of the aromatic components, on the course of the copolycondensation. The experimental procedure was the same as before [1]; the reaction temperature was 65°, the catalyst concentration was 3 moles per cent on the total amount of aromatic compounds, the molar ratio aromatic: dichloroethane was 1.5: 1, and the molar ratios benzene: chlorobenzene were 1:0, 1:1, 1:2, 1:5, 1:10, 1:20, 1:50, and 0:1. The experimental results are given in Tables 1-8 and Figures 1-4.

TABLE 1
Polycondensation of 1,2-Dichloroethane with
Benzene

Duration of reaction (minutes)	Yield of polymer (%)	Molecular weight of polymer	Degree of polymerization
30	9,5	1660	15,9
60	18,5	1720	16,5
90	28,6	1790	17,2
120	38,2	1850	17,8
150	49,6	1970	18,9
180	57,4	2850	27,4
210	63,8	2990	28,7

From Tables 1 and 8 and Fig. 1 it will be seen that polycondensation is considerably more rapid in the chlorobenzene-dichloroethane system (benzene:chlorobenzene = 0:1) than in the benzene-dichloroethane system (benzene: chlorobenzene = 1:0).

On the other hand, the degree of polymerization of the benzene-dichloroethane condensate is higher than that of the chlorobenzene-dichloroethane condensate (Tables 1 and 8).

It is necessary to take account of the fact that in the course of the polycondensation the polymer is formed as a reaction complex and is bound with aluminum chloride in this complex more firmly than any original aromatic reactant is; otherwise, the formation of a polymer would be impossible. In the polycondensation of dichloroethane with benzene the aluminum

chloride complex with the terminal phenyl group of the polymer is apparently more stable than the complex with the terminal chlorophenyl group in the polycondensation product from dichloroethane and chlorobenzene. In the second case the low stability of the complex results in its more ready decomposition into aluminum chloride and polymer under the given reaction conditions, as a result of which the polymer passes into the outer sphere (relative to the complex) and participates to a considerably less extent in the growth of the polymer chain than polyethylenepheryl, the terminal phenyl of which is more firmly bound in the aluminum chloride complex. The differing stabilities of the polymer complexes can, in our opinion, be explained by the fact that in the case of a terminal phenyl group the benzene ring contains only an alkyl substituent, which does not create any steric hindrance to the formation of a complex with aluminum chloride. In the case of a terminal chlorophenyl group, the benzene nucleus contains two substituents, which create some steric hindrance to the

formation of a complex with aluminum chloride and reduce the stability of such a complex. Apart from the effect of the number and positions of the substituents, their polarities are also of importance. In the case of a terminal phenyl group the substituent is polarized positively, so that the benzene ring acquires a negative charge. It is known that aluminum chloride readily reacts with atoms and radicals polarized negatively, forming stable complexes with them. Acid chlorides and ketones form stable complexes with aluminum chloride [3] on account of the presence of an oxygen atom, which has unshared pairs of electrons and forms the negative end of a dipole.

TABLE 2

Copolycondensation of 1,2-Dichloroethane with Benzene and Chlorobenzene (Benzene: Chlorobenzene = 1 : 1)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	10,4	2,06	15,2	106,1	1950	18,4
60	18,8	2,21	14,1	106,3	2200	20,7
90	22,6	2,31	13,4	106,5	2380	22,3
120	27,9	2,66	11,5	106,8	2440	22,8
150	33,9	3,12	9,6	107,2	2550	23,8
180	38,7	3,43	8,6	107,6	2630	24,4
210	44,4	3,49	8,4	107,7	2840	26,6

TABLE 3

Copolycondensation of 1,2-Dichloroethane with Benzene and Chlorobenzene (Benzene: Chlorobenzene = 1 : 2)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	6,3	5,38	5,0	109,8	—	—
60	10,7	6,17	4,2	110,7	1630	14,7
90	16,9	6,56	3,9	111,2	2070	18,6
120	20,4	6,61	3,8	111,2	2610	23,5
150	24,6	6,73	3,7	111,4	2740	24,6
180	29,8	7,48	3,2	112,3	2800	24,9

TABLE 4

Copolycondensation of 1,2-Dichloroethane with Benzene and Chlorobenzene (Benzene: Chlorobenzene = 1 : 5)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	4,5	8,95	2,5	113,9	—	—
60	8,8	10,10	2,0	115,4	1650	14,3
90	13,5	11,38	1,7	116,9	1730	14,8
120	16,3	11,06	1,8	116,5	1740	14,9
150	18,2	12,37	1,5	118,1	2270	19,2
180	22,1	11,75	1,6	117,1	2320	19,8
210	25,0	13,11	1,3	119,2	2510	21,1

In the case of terminal chlorophenyl groups, the benzene nucleus contains oppositely polarized substituents (alkyl group and chlorine atom), which results in a reduction of the negative polarity of the aromatic nucleus and, possibly, even in a change in the sign of this polarity. In both cases the result is lower stability of the aluminum chloride complex with the aromatic nucleus. These views are fully in accord with the known passivating effect of the chlorine atom in chlorobenzene on the aromatic nucleus as shown in electrophilic substitutions.

TABLE 5

Copolycondensation of 1,2-Dichloroethane with Benzene and Chlorobenzene (Benzene: Chlorobenzene = 1: 10)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	8,4	14,57	1,01	121,2	—	—
60	13,2	15,82	0,82	122,9	1540	12,5
90	14,7	16,46	0,74	123,9	2060	16,6
120	21,2	77,21	0,65	124,9	2270	18,2
150	26,9	18,20	0,54	126,4	2300	18,2
180	28,0	18,00	0,56	126,1	2290	18,2
210	30,5	18,57	0,50	126,9	2310	18,2

TABLE 6

Copolycondensation of 1,2-Dichloroethane with Benzene and Chlorobenzene (Benzene: Chlorobenzene = 1: 20)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	8,8	18,41	0,52	126,7	—	—
60	12,0	19,61	0,41	128,3	1430	11,1
90	14,9	20,66	0,32	130,2	1590	12,2
120	19,3	21,46	0,26	131,4	1600	12,2
150	20,9	22,50	0,18	133,2	1630	12,2
180	26,6	22,10	0,21	132,5	2060	15,5
210	34,0	22,69	0,17	133,5	2080	15,6

TABLE 7

Copolycondensation of 1,2-Dichloroethane with Benzene and Chlorobenzene (Benzene: Chlorobenzene = 1: 50)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
60	14,9	22,83	0,16	133,7	1450	10,8
90	21,6	24,46	0,061	136,6	1520	11,1
120	28,5	24,79	0,043	137,0	1600	11,7
150	35,8	25,61	0,000	138,5	1690	12,2
180	38,9	25,25	0,017	137,9	1790	13,0
210	46,1	25,46	0,006	138,3	1860	13,4

The high stability of complexes of aluminum chloride with a terminal phenyl group has the result that in the polycondensation of benzene with dichloroethane, as the duration of the experiment increases, the molecular weights of the polymer molecules increase to a greater extent than the number of such molecules. In the polycondensation system chlorobenzene-dichloroethane, since the terminal chlorophenyl groups forms moderately stable readily dissociating complexes with aluminum chloride, a polymer of low molecular weight is formed. As the aluminum chloride molecules regenerated in the dissociation will again take part in the polycondensation process, the total number of polymer molecules will be greater and the yield of polymer will increase.

As will be seen from Tables 1 and 8 and Fig. 1, in the polycondensation of the system benzene-chlorobenzene-dichloroethane the yield of copolymer and degree of polymerization increase with increase in the duration of reaction for all benzene: chlorobenzene ratios.

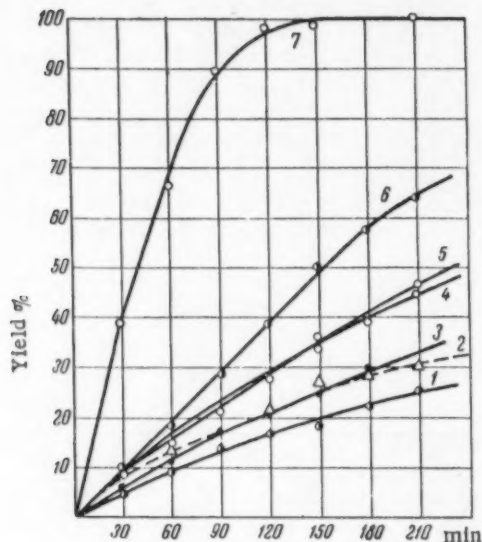


Fig. 1. Relation of yield of copolymer to duration of reaction for benzene:chlorobenzene ratios of 1) 1:5; 2) 1:10; 3) 1:2; 4) 1:1; 5) 1:50; 6) benzene; 7) chlorobenzene.

more rapidly consumed in the course of polycondensation, and as the process proceeds the chlorobenzene content of the system increases, which results in an increase in the chlorine content of the copolymer on account of the

duration of reaction for all benzene: chlorobenzene ratios. Also, it is notable that replacement of part of the benzene by chlorobenzene results in reduced rate of polycondensation, and a minimum yield of copolymer is observed when the benzene content of the mixture of aromatic compounds is 9-17 moles per cent. Further increase in the chlorobenzene content of the system leads to increased yields of copolymer, and a maximum yield of macromolecular products is found when when benzene is completely replaced by chlorobenzene. It is clear from Fig. 2 that the replacement of only 2 moles per cent of the chlorobenzene by benzene results in a considerable reduction of the rate of polycondensation. A similar picture is observed in the copolymerization of some binary mixtures of unsaturated compounds [4,5], when the addition of small amounts of a fairly rapidly polymerizing monomer to another monomer that is also readily polymerized leads to a reduction in the rate of reaction; the reduction in rate of copolymerization proceeds until a definite minimum is reached, and further addition of the second monomer then results in an increase in the rate of the process.

It will be seen from Tables 1-8 that at all benzene: chlorobenzene ratios the chlorine content of the copolymer increases as the duration of reaction increases. This, as stated previously [1,2], shows that benzene is

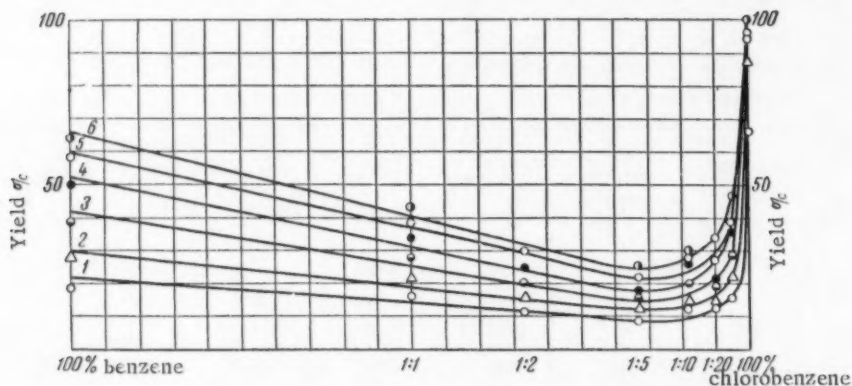


Fig. 2. Relation of yield of copolymer to ratio of aromatic reactants: 1) 60 minutes; 2) 90 minutes; 3) 120 minutes; 4) 150 minutes; 5) 180 minutes; 6) 210 minutes.

higher content of chlorobenzene in the reaction mixture at the given moment, as compared with its content in the original mixture. In the stages of formation of the ternary complex and of intracomplex interaction, both benzene and chlorobenzene take part, but as the relative activity of benzene is considerably higher it participates in these processes to a greater extent than might have been supposed on the basis of the relative amounts of aromatic compounds in the original mixture.

On the basis of the experimental data given above it may be considered that when benzene:chlorobenzene = 1: 10 chlorobenzene and benzene enter into the chain of the polymer at approximately equal rates (in the early stages of the process). Let us try to imagine why replacement of chlorobenzene by benzene to such a small extent leads to such a sharp fall in the yield of copolymer (Fig. 2). When the proportion of the more active component (benzene) of the aromatic mixture is small, in the first stages of polycondensation it is consumed in the formation of copolymer having the highest possible content of ethylenepheryl residues under the given conditions. The copolymer formed gives stable complexes with aluminum chloride. The rate of reaction of these complexes with chlorobenzene is relatively low, since chlorobenzene is the less active aromatic compound.

The rate of reaction of these complexes with benzene is also low, because of the very low concentration of benzene. As a result, at benzene : chlorobenzene ratios of 1: 5 and 1: 10 polycondensation proceeds at a minimum rate. When the benzene content of the reaction mixture is very low (about 2 moles per cent of the total aromatics), the copolymer containing the maximum content of polyethylenepheryl residues formed in the early stages of the process does not bind all the aluminum chloride present in the system, but only part of it. The remaining aluminum chloride initiates the growth of chains formed by the polycondensation of chlorobenzene with dichloroethane. In this case the later stage in the polycondensation can be regarded as the polycondensation of the chlorobenzene-dichloroethane system, which proceeds very rapidly, as indicated above. This is indicated by the fact that in this case n/m is almost zero and the chlorine content of the polycondensation product is that of polyethylenechlorophenyl. (Table 7).

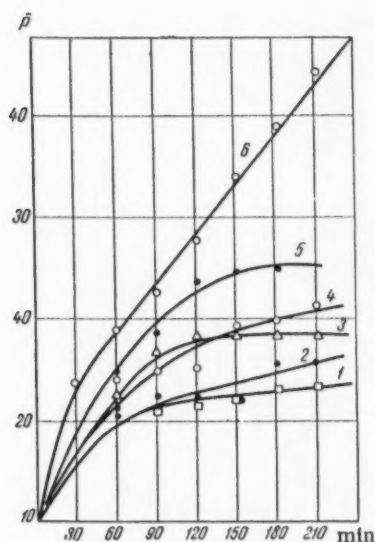


Fig. 3. Relation of degree of polymerization to duration of reaction for benzene : chlorobenzene ratios of 1) 1: 50; 2) 1: 20; 3) 1: 10; 4) 1: 5; 5) 1: 2; 6) 1: 1.

for the sharp reduction in the rate of the process because of the withdrawal of part of the aluminum chloride as a complex with terminal phenyl groups, and the yield of polymer will not attain the values characteristic for this binary system. As the content of the more active component of the reaction mixture (benzene) increases, the rate of the process will, of course, also increase. Hence, in the copolycondensation of dichloroethane with benzene and chlorobenzene the rate of the process is determined by the relative rates of reactions of growing polymer chains with benzene and chlorobenzene proceeding within the complex formed by aluminum chloride, polymer, and components of the reaction system. It follows that the main component, the content of which determines the over-all rate of the copolycondensation process (at constant catalyst concentration), is benzene, the concentration of which determines the numbers of terminal phenyl groups and ethylenepheryl residues in the copolymer chains.

We shall suppose that the relative activity of chlorobenzene r (the activity of benzene being taken as unity) with respect to a growing polymer chain containing the end group $\dots \text{CH}_2\text{CH}_2\text{Cl}$ is given quantitatively by

It may be supposed also that the copolymer formed in the early stages will bind aluminum chloride more weakly in the form of a complex, because most of the molecules of this copolymer will have terminal chlorophenyl groups. Increase in the rate of reaction as a result of transition to the chlorobenzene-dichloroethane polycondensation system cannot compensate completely

$$r = \frac{n_0 / m_0}{n / m},$$

in which n_0/m_0 is the benzene : chlorobenzene ratio in the original mixture and n/m is the experimentally found ratio of benzene and chlorobenzene residues in the copolymer obtained at an early stage of the polycondensation process. The mean value found for r is 0.10 ± 0.02 . Hence, the relative activity of benzene is about ten times as great as that of chlorobenzene in the reaction of dichloroethane with a mixture of benzene and chlorobenzene under the reaction conditions described at the beginning of this paper. It was shown, therefore, that the relative activities of aromatic compounds in the system benzene-chlorobenzene-dichloroethane do not depend on their original relative amounts in the system.

TABLE 8
Polycondensation of dichloroethane with chlorobenzene

Duration of reaction (minutes)	Yield of polymer (%)	Molecular weight of polymer	Degree of polymerization
30	36,8	1560	11,3
60	66,5	1770	12,8
90	88,9	1880	13,6
120	97,6	1880	13,6
150	98,4	1920	13,9
210	100,0	1880	13,6

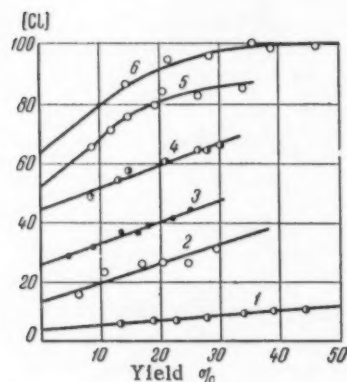


Fig. 4. Relation of the content of $-\text{C}_6\text{H}_3\text{ClCH}_2\text{CH}_2-$ fragments in the copolymer to the yield for benzene:chlorobenzene ratios of 1) 1 : 1; 2) 1 : 2; 3) 1 : 5; 4) 1 : 10; 5) 1 : 20; 6) 1 : 50.

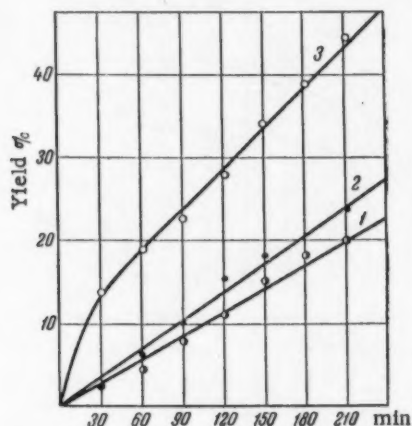


Fig. 5. Relation of yield of copolymer to duration of reaction for aromatics: dichloroethane ratios of 1) 1.2 : 1; 2) 1.3 : 1; 3) 1.5 : 1.

It will be seen from Fig. 3, that, as the chlorobenzene content of the system increases, the degree of polymerization of the copolymer formed falls. This is to be expected, for, in the separate polycondensations with dichloroethane, polymers obtained from chlorobenzene have a lower degree of polymerization than polymers formed from benzene.

In Fig. 4 the composition of copolymers obtained from the system benzene-chlorobenzene-dichloroethane is shown as a function of yield. Fig. 4 shows that there is a linear relationship between yield of copolymer and the content of ethylenechlorophenyl residues when the benzene : chlorobenzene ratio is from 1 : 1 to 1 : 10.

Moreover, for benzene : chlorobenzene ratios from 1 : 2 to 1 : 10 these linear relationships are characterized by constant slope, while the "constant" term varies in regular fashion. Mathematical treatment of these results in the range of benzene : chlorobenzene ratios from 1 : 10 to 1 : 2 enabled us to express the relationship by

$$B = 0.66 A + 4.5 (1 + C).$$

in which A is the yield of copolymer (%), B is the content of ethylenechlorophenyl residues in the copolymer (moles %), and C is the chlorobenzene : benzene molar ratio in the original mixture. For a system containing equimolecular amounts of chlorobenzene and benzene this equation becomes

$$B = 0.15 A + 4.5.$$

The experimental and calculated values are in close agreement. When the chlorobenzene content of the system is very high there is no longer a linear relationship between the yield of copolymer and the content of ethylenechlorophenyl residues in the copolymer.

TABLE 9

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene (Aromatics :
: dichloroethane = 1.2 : 1)

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
60	4,6	2,13	14,7	106,2	—	—
90	7,9	2,34	13,2	106,5	1780	16,7
120	11,1	2,73	11,1	106,9	2180	20,4
150	15,1	2,90	10,4	107,0	2170	20,3
180	18,1	3,06	9,8	107,2	2300	21,4
210	20,2	3,64	8,0	107,9	2380	22,1

TABLE 10

Copolycondensation of Dichloroethane with Benzene and Chlorobenzene (Aromatics :
: dichloroethane = 1.3 : 1).

Duration of reaction (minutes)	Yield of polymer (%)	Chlorine content of copolymer (statistical mean)	n/m	Basal mole of copolymer (statistical mean)	Molecular weight of copolymer	Degree of polymerization
30	2,3	2,50	12,3	—	—	—
60	6,0	2,37	13,0	106,5	—	—
90	10,1	2,74	11,1	106,9	2060	19,3
120	15,4	2,45	12,5	106,5	2180	20,4
150	18,1	2,95	10,2	107,0	2190	20,4
210	23,7	3,90	7,4	108,1	2370	21,9

By the use of the above equations it is possible to calculate the composition of a copolymer as a function of its yield at constant aromatics : dichloroethane ratio over a fairly wide range of compositions of the aromatic mixture (33.3-9 moles per cent of benzene). As the yield of copolymer is determined also by the duration of reaction under given conditions, it is therefore possible to obtain a copolymer of desired composition by change in a) the benzene : chlorobenzene ratio in the original mixture, b) the duration of polycondensation at constant benzene : chlorobenzene ratio, and c) both duration of reaction and also the benzene : chlorobenzene ratio in the original mixture, simultaneously.

In order to determine the effect of the aromatics : dichloroethane ratio on the course of polycondensation in the system benzene-chlorobenzene-dichloroethane, experiments were carried out in which this molar ratio

had the values 1.2 : 1, 1.3 : 1, and 1.5 : 1. All other conditions were kept constant: the benzene : chlorobenzene molar ratio was 1 : 1, the concentration of aluminum chloride was 3 moles per cent on the total aromatics, and the reaction temperature was 65°. The results of these experiments are given in Tables 9 and 10 (see also Table 2).

From Tables 2, 9 and 10 and Fig. 5 it will be seen that for all the investigated aromatics : dichloroethane ratios the yield of copolymer increases with increase in the duration of reaction. Increase in the dichloroethane content of the reaction mixture leads to reduced yield of copolymer. This reduction in the yield of copolymer can be explained by the fact that in this case dichloroethane acts as a diluent, so that the rate of the polycondensation process is reduced.

In all our experiments, with increase in the duration of reaction the chlorine content of the copolymer increases and the ratio n/m falls correspondingly. Comparison of values of n/m in the initial stages of the process shows that this ratio does not depend on the aromatics: dichloroethane ratio (within the limits of experimental error), so that increase in the dichloroethane content of the reaction mixture has no effect on the relative activities of benzene and chlorobenzene in their copolycondensation with dichloroethane in presence of aluminum chloride.

Hence, we have established, for the first time for copolycondensation products, a relationship between the composition of the copolymer and the conditions under which the process is carried out. The relations found are, of course, not all-embracing and are applicable only within certain limits; the results, however, enable us to suggest that quantitative relationships may be established in the future which will cover more parameters than the equations given above.

SUMMARY

1. The effect of the original proportions of reactants on the course of the copolycondensation of 1,2-dichloroethane with benzene and chlorobenzene was studied.
2. The relative activity of chlorobenzene was determined (the activity of benzene being taken as unity), and it was shown that the relative activities of these aromatic compounds do not depend on their concentrations in the original mixture.
3. An empirical equation was found for the composition of the copolymer as a function of its yield and the relative amounts of aromatic compounds in the original mixture.
4. Increase in the dichloroethane content of the reaction mixture results in reduced yield of copolymer.

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HETEROCHAIN POLYESTERS

COMMUNICATION 11. CHEMICAL DEGRADATION OF POLYETHYLENE TEREPHTHALATE

V. V. Korshak, N. I. Bekasova, and V. A. Zamlatina

Polyethylene terephthalate and products prepared from it (fiber, film) have high chemical stability under the conditions to which they are normally subjected in use. This property is to be attributed to their physical state rather than to the chemical nature of polyethylene terephthalate itself. Being a polyester, polyethylene terephthalate should undergo the chemical reactions peculiar to this class of compounds. In order to verify this we investigated the behavior of polyethylene terephthalate when heated in cresol solution, and we also carried out its acidolysis and glycolysis.

EXPERIMENTAL

Degradation of Polyethylene Terephthalate in Cresol Solution. The instability of solutions of polyethylene terephthalate in m-cresol at 100-130° was noted by Gordijenko [1]. We investigated the change in viscosity of a 0.5% solution of the polyester in cresol (mixture of isomers) in an atmosphere of nitrogen when maintained for a long time in the temperature range 110-205°. Having shown that the viscosity of the solution is greatly reduced by exposure to high temperatures, i.e. that the substance is degraded, we isolated the degradation product and investigated its properties with the object of obtaining an idea of the mechanism of this process.

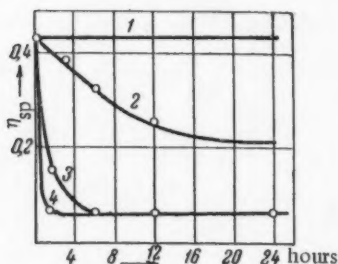


Fig. 1. Degradation of polyethylene terephthalate in cresol solution at 1) 110°; 2) 132°; 3) 170°; 4) 205°.

a reduction in specific viscosity which increases in rapidity as the temperature is raised.

It was shown by special experiments that the viscosity of the pure solvent does not change when heated under the same conditions.

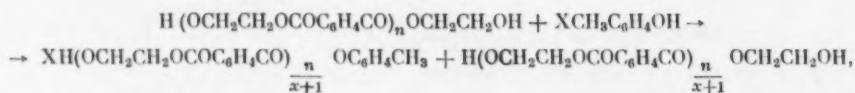
In order to study the properties of the degradation product we prepared a 5-g sample, for which purpose the polyester was refluxed with 100 parts of p-cresol for six hours. When the solution was cool, the substance

The change in the viscosity of the solution was determined as follows. A 100-ml round-bottomed flask was fitted with reflux condenser and tube for the passage of nitrogen (which passed through the condenser); 50 ml of a 0.5% solution of the polyester in cresol, having a specific viscosity of 0.43, was introduced into the flask. Air was displaced by nitrogen, and the flask was immersed in a metal bath at the required temperature. At definite intervals of time the flask was removed from the bath, the solution was cooled, and its viscosity was determined with an Ostwald viscometer at 20°.

The results of these investigations are shown in Fig. 1, and from these it may be concluded that at 100° a cresol solution of polyethylene terephthalate is still quite stable, whereas at higher temperatures there is

was precipitated with petroleum ether, filtered off, and purified by Soxhlet extraction with petroleum ether. After being dried at 70° the substance melted at 226-232°; it was purified by crystallization from tetrachloroethane, but its melting point remained unaltered. The specific viscosity of the 0.5% solution of this substance in cresol was 0.06.

The terminal hydroxy groups of the degradation product were bromoacetylated with bromoacetyl bromide by Griehl and Noul's method [2]. The bromine content of the product was determined by the Volhard method [3, 4]; values of 2.86 and 2.68% were obtained. On the assumption that the degradation of the polyester in cresol proceeds by phenolysis occurring in this case by the scheme



we calculated the mean molecular weight of the product on the assumption (not altogether precise) that there is one hydroxy group in each newly formed molecule. The calculation was carried out by the equation

$$M = \frac{80 \cdot 100}{2.77} - 121 = 2767,$$

in which 80 is the atomic weight of bromine, 2.77 is the mean bromine content (%), and 121 is the weight of the bromoacetyl residue.

This molecular weight corresponds to a polyester consisting of 14 repeating units and one cresol residue: for $\text{H}(\text{OCH}_2\text{CH}_2\text{OCOC}_6\text{H}_4\text{CO})_{14}\text{OC}_6\text{H}_4\text{CH}_3$ M - is 2798.

The elementary analysis of the substance corresponded fairly closely to the composition of this polyester:

Found %: C 62.79; 62.86; H 4.43; 4.39 $\text{C}_{147}\text{H}_{120}\text{O}_{57}$. Calculated % C 63.09; H 4.31.

Acidolysis and Glycolysis of Polyethylene Terephthalate. The acidolysis reaction was first discovered by one of us in collaboration with Rafikov and Pinkina [5, 6] for the case of polyamides; it was studied in detail by us for the case of the reaction of polyhexamethylenedipamide with adipic and stearic acids added in amounts ranging from 0 to 100 moles per cent [7]. In collaboration with Golubev we studied the acidolysis of the polyester formed by adipic acid with ethylene glycol under the action of various amounts of adipic acid, and we studied also the glycolysis of this polyester with ethylene glycol [8]. The kinetics of the glycolysis and alcoholysis of polydecamethylene adipate under the action of small amounts of 1,10-decanediol and lauric acid were investigated by Flory [9]. One of us and Vinogradova [10] investigated the alcoholysis of polyhexamethylene sebacate with hexadecyl alcohol.

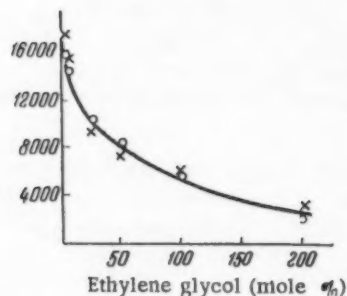


Fig. 2. Glycolysis of polyethylene terephthalate.

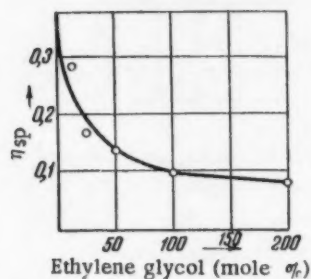


Fig. 3. Acidolysis of polyethylene terephthalate.

Soviet investigators have established various laws governing the degradation of polyesters and polyamides under the action of acids and glycols. It was shown that the longest molecules are preferentially degraded and

the extent of degradation is directly proportional to the amount of degrading agent. The reaction has a reversible and equilibrium character, and the degrading agent is therefore not utilized completely. These regularities are of great importance for the understanding of the polycondensation of bifunctional compounds.

We investigated the acidolysis and glycolysis of polyethylene terephthalate with adipic acid and ethylene glycol. The reaction was carried out in biphenyl solution at 200°; under these conditions the polyester is readily soluble in biphenyl and undergoes no change in solution. At a higher temperature biphenyl (b.p. 255°) begins to sublime appreciably.

Procedure. The original polyethylene terephthalate was purified by precipitation from cresol with methanol. Traces of cresol were removed by Soxhlet extraction with methanol. The resulting sample had a specific viscosity of 0.33 as a 0.5% solution in cresol. The biphenyl was vacuum-sublimed. Ethylene glycol was distilled twice over sodium, and adipic acid (m.p. 151°) was recrystallized from water.

Polyethylene terephthalate (1 g) biphenyl (50 g), and ethylene glycol or adipic acid (a definite molar percentage calculated on one repeating unit, the weight of which is 192), were mixed in a 100 ml round-bottomed flask. The flask was purged with dry nitrogen and lowered into a metal bath at 200°. After being heated for six hours, the flask was removed and, when cool, its contents were treated with petroleum ether. In the case of glycolysis the precipitate consisted solely of the degradation product, and in the case of acidolysis it contained also unchanged adipic acid. The adipic acid was then separated from the degradation product by extraction with ethanol, in which it was quantitatively titrated with 0.2 N NaOH. The specific viscosity of the degradation product as a 0.5% solution in cresol at 20° was determined. Its viscosimetric molecular weight was calculated from Mark and Hauwink's formula [11] with the coefficients proposed for polyethylene terephthalate by Turska-Kusmierz and Skwarski [12]:

$$[\eta] = K_m \cdot M^\alpha = 5,517 \cdot 10^{-4} M^{0.708},$$

in which

$$[\eta] = \frac{\frac{\eta_{sp}}{c}}{1 + 0,66 \eta_{sp}},$$

In our case the concentration c (%) is 0.5.

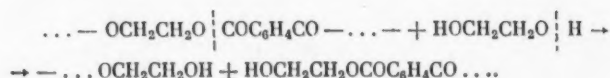
For a more complete characterization we determined also the terminal hydroxy groups by bromoacetylation. The molecular weight was calculated for molecules containing two hydroxy groups by the equation

$$M = \frac{160 \cdot 100}{\% \text{ Br}} - 242$$

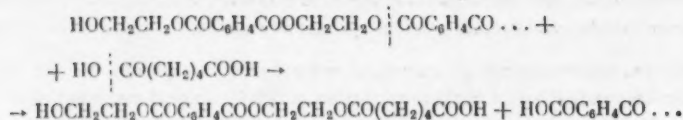
We made an attempt to determine terminal carboxy groups in the acidolysis products by Pohl's method [13], i.e. titration of a sample in benzyl alcohol, but it was found that boiling brought about further degradation rather than dissolution. The results of the experiments are given in Figures 2 and 3.

Our results show that the extent of the degradation of the polyester increases with increase in the amount of added ethylene glycol or adipic acid, which confirms the rule noted previously, i.e. that the tendency for macromolecular compounds to undergo degradation is proportional to the sizes of their molecules [14].

In the case of glycolysis, all newly formed molecules have hydroxy groups at their ends, a fact which is proved by their acylation. This confirms that, in the case of polyethylene terephthalate, glycolysis proceeds in accordance with the equation:



In the case of acidolysis, the total number of hydroxy groups remains constant, which is in accord with the following scheme for this reaction:



SUMMARY

1. An investigation was made of the degradation of polyethylene terephthalate in cresol solution at various temperatures. It was shown that above 110° the polyester is degraded. A suggestion was made concerning the cause of the degradation.

2. A study was made of the acidolysis and glycolysis of polyethylene terephthalate in biphenyl solution at 200° under the action of adipic acid and ethylene glycol. It was shown that the extent of the degradation increases with increase in the amount of degrading agent. The degradation products were characterized.

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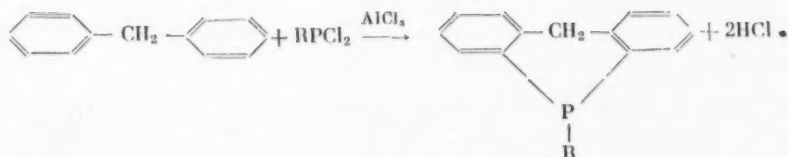
ORGANOPHOSPHORUS POLYMERS

COMMUNICATION 3. POLYCONDENSATION OF DICHLORO (p-CHLOROPHENYL) PHOSPHINE WITH BIBENZYL

V. V. Korshak, G. S. Kolesnikov, and B. A. Zhubanov

Phosphorus-containing macromolecular compounds in which phosphorus is in the main chain of the polymer and is directly united with carbon atoms have received very little study, and there are references in the literature only to products of the copolymerization of unsaturated compounds with dichlorophosphines, in which the main chain consists of carbon and phosphorus atoms [1, 2]. The lack of attention to polymers of this type prompted us to undertake the present investigation.

Aryldichlorophosphines are bifunctional compounds containing reactive chlorine atoms capable of participating in various reactions, including reactions with aromatic compounds in presence of aluminum halides. We attempted to synthesize macromolecular organophosphorus compounds by the reaction of dichloro (p-chlorophenyl) phosphine with aromatic hydrocarbons in presence of aluminum chloride in the hope that dichloro(p-chlorophenyl)phosphine would behave like 1,2-dichloroethane or methylene chloride. We have shown previously that these dichloroalkanes react with benzene and other aromatic compounds with the formation of macromolecular polycondensation products [3-12]. It was found, however, that the reaction of dichloro(p-chlorophenyl)phosphine with benzene in presence of aluminum chloride does not result in the formation of polymers. This indicates that the replacement of a hydrogen atom in benzene by a phosphorus-containing group with formation of a C-P bond results in the deactivation of the remaining hydrogen atoms of the benzene ring, so that further substitution becomes either impossible or extremely difficult. The deactivation of hydrogen atoms in benzene rings attached to a phosphorus atom is indicated also by the fact that triphenylphosphine, according to our observations, does not undergo polycondensation with 1,2-dichloroethane in presence of aluminum chloride. We supposed that in bibenzyl this deactivating effect of the C-P bond should not be observed, because the aromatic nuclei of this compound are separated by the $-\text{CH}_2\text{CH}_2-$ bridge and any mutual effects of the nuclei and the substituents in these nuclei should be weak. It would have been possible to take biphenyl or diphenylmethane as the aromatic hydrocarbon, but the polycondensation could then be complicated by the formation of five- and six-membered rings, e. g.



Dichloro (p-chlorophenyl)phosphine was prepared by Buchner and Lockhart's method [13] from phosphorus trichloride and chlorobenzene in presence of aluminum chloride; the yield was 54%. In a much lower over-all yield we prepared dichloro (p-chlorophenyl)phosphine by the method proposed by Iakubovich and Motsarev [14]; yield about 15% on the amount of 1-bromo-4-chlorobenzene taken.

In order to determine the effect of catalyst concentration on the course of the polycondensation of dichloro-(p-chlorophenyl)phosphine with bibenzyl we carried out a series of experiments in which the molar ratio of

reactants was 1 : 1, reaction was for three hours, and the temperature was 150°. The concentration of aluminum chloride was varied from 10 to 50 mole per cent on the amount of bibenzyl. The results are given in Table 1. The molecular weights of the polymers were characterized by the ratio η_{sp}/c , in which η_{sp} was the specific viscosity of the solution of the polymer in benzene and c was the concentration of the solution of polymer (g/100 ml).

TABLE 1
Polycondensation of Dichloro(p-chlorophenyl)phosphine with Bibenzyl

Ex- per- iment	Catalyst con- centration (mole % on bibenzyl)	Yield of polymer (%)	η_{sp}/c	Biphenyl re- covered un- changed (% of original amount)
1	10	Reaction did not go		
2	20	38,8	0,040	70,2
3	30	47,0	0,042	56,0
4	40	48,2	0,038	47,8
5	50	47,9	0,043	32,4

TABLE 2
Polycondensation of Dichloro(p-chlorophenyl)phosphine with Bibenzyl

Ex- per- iment	Catalyst con- centration (mole % on bibenzyl)	Yield of polymer (%)	η_{sp}/c	Biphenyl recovered unchanged (% of original amount)
6	1	40,7	0,038	54,4
7	2	40,7	0,046	57,7
3	3	47,0	0,042	56,0
8	4	42,0	0,044	56,6
9	5	42,5	0,047	55,0

It will be seen from Table 1 that with increase in catalyst concentration the yield of polymer rises at first and then becomes constant, whereas η_{sp}/c remains almost constant and the amount of bibenzyl remaining unchanged is reduced. According to the results of this series of experiments increase in the concentration of aluminum chloride to beyond 30 mole per cent does not result in increase in the yield of polymer.

The second series of experiments was carried out with the object of determining the effect of the duration of the reaction on the yield and molecular weight of the polymer. In this series the dichloro (p-chlorophenyl) phosphine : bibenzyl ratio was kept constant at 1 : 1, the aluminum chloride concentration was 25 mole per cent on the amount of bibenzyl, the reaction temperature was 150°, and the duration of the reaction was varied from one to five hours. The results of this series of experiments are given in Table 2.

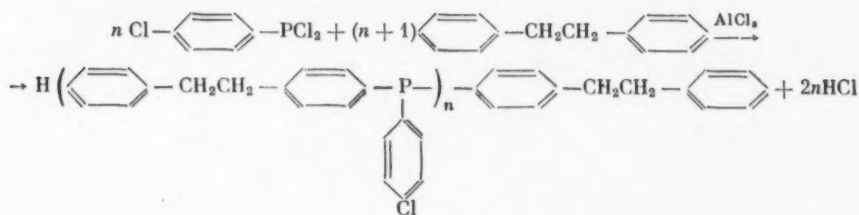
These results show that increase in the duration of the reaction from one to five hours scarcely affects the character of the process under the given conditions.

With the object of determining the effect of temperature on the yield and molecular weight of polymer we carried out a third series of experiments in which the dichloro (p-chlorophenyl) phosphine : bibenzyl molar ratio was kept constant at 1 : 1, the aluminum chloride concentration was 30 moles per cent on the amount of bibenzyl, the duration of the reaction was three hours, and the reaction temperature was varied from 150° to 225°. The results of this series are given in Table 3.

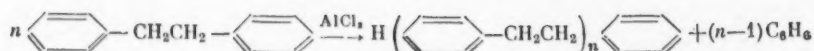
It will be seen from Table 3 that the reaction temperature has an appreciable effect on the course of the polycondensation of dichloro (p-chlorophenyl) phosphine with bibenzyl. With rise in temperature from 150° to 200° the yield of polymer remains almost constant, but its molecular weight rises to a maximum at 200°. Further rise in temperature to 225° results in a sharp fall in the yield of polymer and in its molecular weight; at the same time the amount of unchanged bibenzyl also diminishes rapidly.

The following facts emerge from an examination of the results given in Tables 1 and 3. Table 1 shows that increase in aluminum chloride concentration to 50 mole per cent results in reduction in the amount of unchanged bibenzyl, although the yield of polymer remains constant. Rise in reaction temperature to 225° (Table 3) leads not only to reduced yield of polymer, but also a sharp reduction in the amount of unchanged bibenzyl, which can be explained, in our opinion, as follows. In addition to the polycondensation of dichloro(p-chlorophenyl)phosphine with formation of a phosphorus-containing heterochain polymer, in presence of aluminum chloride there may occur also some transarylation of bibenzyl with formation of polyethylenephényl, as observed by two of us [15]. In the polycondensation of dichloro(p-chlorophenyl)phosphine with bibenzyl in presence of aluminum chloride, the following reactions may occur.

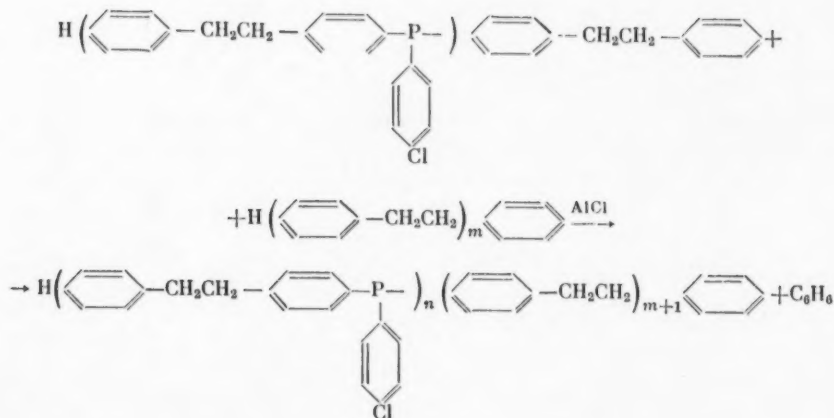
1. The polycondensation of dichloro(p-chlorophenyl)phosphine with bibenzyl:



2. The transarylation of bibenzyl:

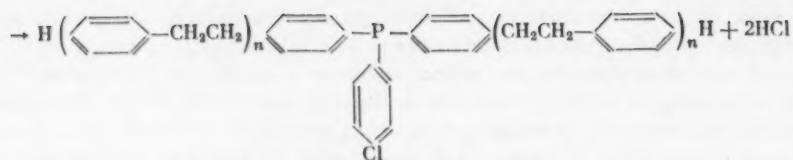


3. The reaction of growing chains of the heterochain phosphorus-containing polymer with polyethylenephényl by a process of the transarylation type:

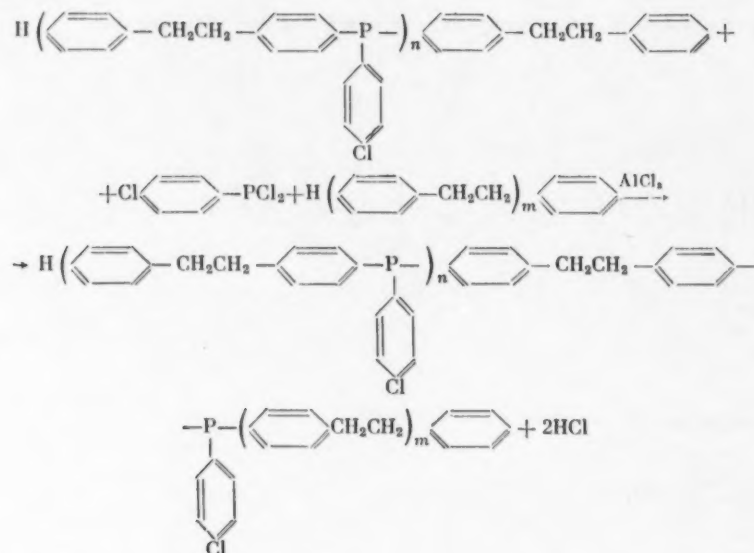


4. Reaction of dichloro(p-chlorophenyl) phosphine with polyethylenephényl:

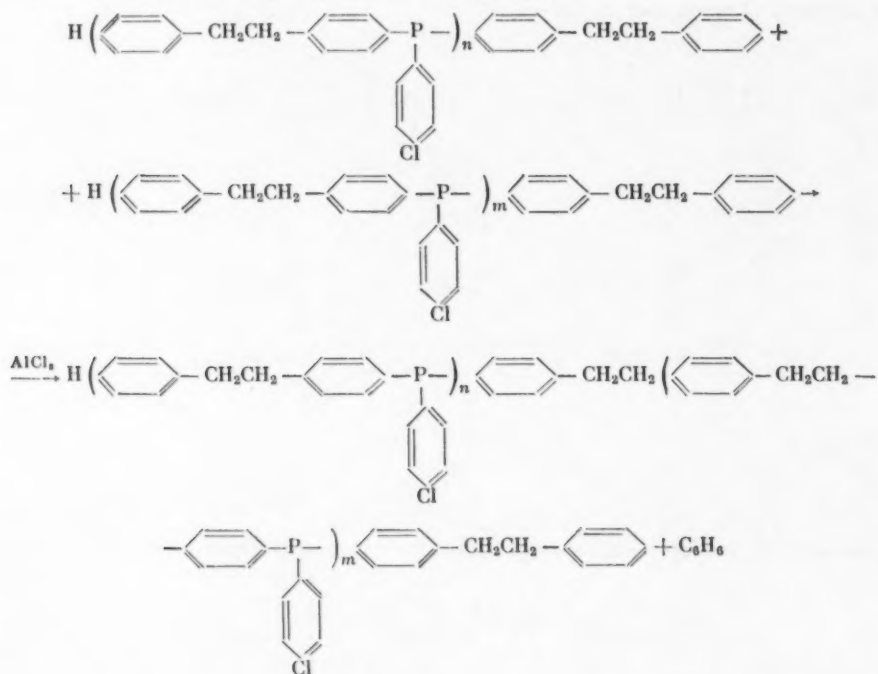




5. Reaction of dichloro(p-chlorophenyl)phosphine with the heterochain phosphorus-containing polymer and polyethylenephenyl:



6. Transarylation of molecules of phosphorus-containing polymer:



All these reactions probably proceed simultaneously, and this results in the formation of a heterochain organophosphorus polymer containing fragments of the carbon-chain polymer polyethylenephényl; the resulting polymer is a copolymer containing the units

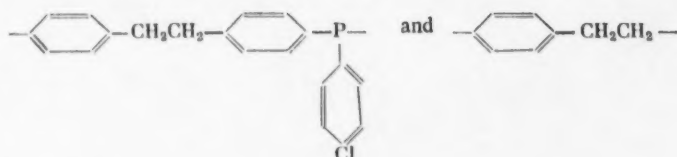


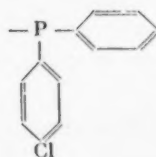
TABLE 3

Polycondensation of Dichloro(p-chlorophenyl)phosphine with Bibenzyl

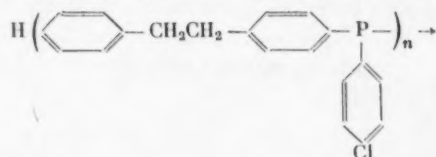
Ex- peri- ment	Catalyst con- centration (mole % on bibenzyl)	Yield of polymer (%)	n_{sp}/c	Biphenyl recovered unchanged (% of original amount)
5	150	47,0	0,042	56,0
10	175	40,4	0,043	55,5
11	190	40,7	0,044	52,1
12	200	41,0	0,064	41,2
13	225	21,1	0,035	15,4

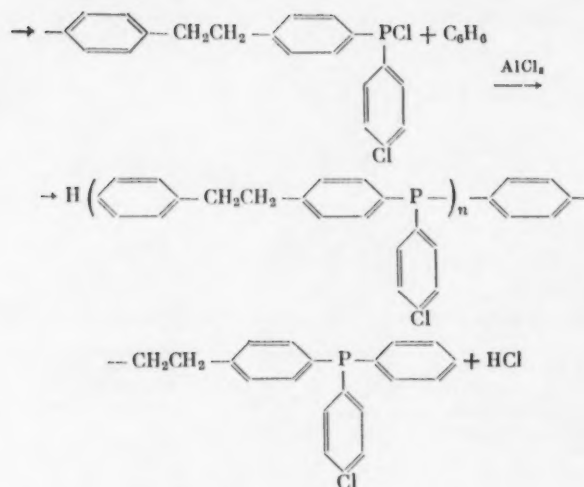
If these suggestions are true, polymers prepared under different conditions should be different in composition. In those cases in which bibenzyl not only reacts with dichloro(p-chlorophenyl)phosphine, but also takes part in the transarylation reaction, the carbon content of the polymer should be greater and the phosphorus and chlorine contents should be less than in the absence of the transarylation reaction. The results on the carbon, hydrogen, and chlorine contents of the polymers show that the composition of the polymers depends on the conditions of preparation (Table 4).

It will be seen from Table 4 that increase in catalyst concentration (Experiments 2-5) leads to increased carbon content and reduced chlorine content, which indicates increase in the importance of the part played by transarylation as the catalyst concentration is increased. With rise in reaction temperature there is a reduction in the chlorine content and an increase in the carbon content of the polymer, which again indicates increased participation of transarylation in the polycondensation process. Since transarylation leads to the formation of benzene, which takes no part in the polycondensation, the yield of polycondensation products and the amount of unchanged bibenzyl diminish. The presence of benzene in the reaction mixture leads to the formation of unreactive end groups



which results from the reaction of benzene with the growing polymer molecule; chain growth is therefore stopped, and there is a resulting reduction in the yield of polymer and in its molecular weight:





Moreover, benzene can degrade the polymer formed, which will again result in a reduction in the molecular weight of the polymer.

TABLE 4
Compositions of Polymers obtained by the Polycondensation of
Dichloro (p-chlorophenyl)phosphine with Bibenzyl

Experi- ment	Found %					
	C		H		Cl	
2	55,14	55,12	4,13	4,16	13,45	13,43
3	53,75	53,94	4,05	4,19	13,15	13,19
4	59,00	58,95	4,76	4,60	12,94	12,43
5	—		—		8,37	8,38
10	57,16	56,92	4,22	4,10	12,97	13,12
12	62,21	62,15	4,37	4,43	11,75	11,85
13	67,43	67,70	4,55	4,63	8,25	8,16

The results show that with rise in temperature and increase in catalyst concentration the rate of transarylation increases more rapidly than the rate of polycondensation, and the proportion of $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2-$ fragments in the polymer is increased.

It should be noted that the composition of polycondensation products obtained at constant ratio of reactants, constant catalyst concentration, and constant temperature (150°), but with different durations of reaction is almost constant.

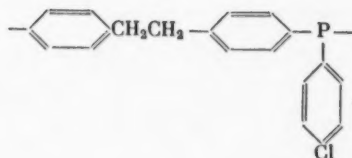
In order to determine the effect of the ratio of reactants on the yield, molecular weight, and composition of the polycondensation, we carried out a series of experiments in which the temperature was 200° , the duration of reaction was three hours, the aluminum chloride concentration was 30 mole per cent on the amount of bibenzyl, but the dichloro (p-chlorophenyl)phosphine : bibenzyl ratio was varied from 1 : 1 to 1 : 2. The results of this series of experiments are given in Table 5.

TABLE 5
Polycondensation of Dichloro (p-chlorophenyl)phosphine with Bibenzyl

Ex-periment	Dichloro(p-chloro-phenyl)phosphine: bibenzyl molar ratio	Yield of polymer (%)	η_{sp}/c	Found %		
				C	H	Cl
12	1 : 1	41,0	0,064	62,21	4,37	11,75
				62,15	4,43	11,85
14	1 : 1,25	55,8	0,036	63,24	4,74	10,09
				63,48	4,76	10,17
15	1 : 1,5	98,0	0,032	66,50	5,03	11,11
				66,38	5,00	10,89
16	1 : 2	81,0	0,029	70,19	5,21	9,50
				70,39	5,24	9,51

It will be seen from Table 5 that increase in the bibenzyl content of the reaction mixture leads to increase in the yield of polymer and reduction in its molecular weight. Increase in the yield of polymer with increase in the bibenzyl content of the reaction mixture is to be explained by the fact that in this case the dichloro (p-chlorophenyl)-phosphine reacts more completely and the part played by transarylation in polymer formation increases. Confirmation of this is provided by the increase in carbon content with increase in the bibenzyl content of the original mixture. Reduction in molecular weight with increase in the bibenzyl content of the reaction mixture is quite in accordance with the regularities observed in such processes. It is known [16] that, when one component of a reaction system is in excess, the molecular weight of the macromolecular compound formed is the lower, the greater this excess.

On examination of the analytical results it will be noted that the chlorine contents of the polymers are generally a little greater than the theoretical value (10.99%) for the chlorine content of a polymer consisting only of the repeating units



whereas the carbon content is lower than the theoretical value (74.49%). In our opinion, the increase in the chlorine content is to be explained on the view that, in presence of aluminum chloride, the above reactions are accompanied by the migration of chlorine from some dichloro (p-chlorophenyl)phosphine molecules to others and to molecules of already formed polymer. The migration of halogen from one organic compound to another in presence of aluminum chloride is well known.

SUMMARY

1. A study was made of the polycondensation of dichloro (p-chlorophenyl)phosphine with bibenzyl in presence of aluminum chloride, and the main laws of the polycondensation process were established.
2. The replacement of a hydrogen atom in benzene by a phosphorus-containing group with formation of a C-P bond results in the deactivation of the other hydrogen atoms in the benzene ring.
3. The polycondensation of dichloro (p-chlorophenyl)phosphine with bibenzyl is complicated by processes of the transarylation type.

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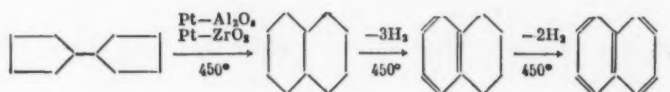
BRIEF COMMUNICATIONS

CATALYTIC ISOMERIZATION OF BICYCLOPENTYL IN PRESENCE OF HYDROGEN UNDER PRESSURE

N. I. Shuikin, M. I. Cherkashin, and G. K. Galvoronskaia

The study of the catalytic transformations of bicyclic systems has resulted in the establishment of some important regularities. Thus, Zelinskii and Tits [1] observed the enlargement of the bicyclopentyl system into the decahydronaphthalene system in the case of the action of hydriodic acid on cyclopentylcyclopentanol. One of us [2] has found that under the action of zinc chloride 2-cyclopentylcyclopentanol gives 1,2,3,4,5,6,7,8-octahydronaphthalene. Similar results were obtained by Turova-Poliak and co-workers [3] for the dehydration of the same alcohol with concentrated phosphoric acid. The same authors [3] succeeded in obtaining trans-decahydronaphthalene by the action of aluminum chloride on bicyclopentyl. Eventova [4] showed that, in presence of platinized charcoal at 310-320°, bicyclopentyl undergoes hydrogenolysis with formation of a complex mixture of hydrocarbons.

In the present investigation we studied the behavior of bicyclopentyl at high temperatures in presence of platinum catalysts and hydrogen under pressure. It was found that under these conditions bicyclopentyl undergoes mainly isomerization into decahydronaphthalene with subsequent dehydrogenation into 1,2,3,4-tetrahydronaphthalene and naphthalene:



EXPERIMENTAL

Bicyclopentyl was synthesized as follows:



The product was distilled through a column; it then had b.p. 55.5° (22 mm) and 189° (753 mm), and it had n_D^{20} 1.4642 and d_4^{20} 0.8650. The literature [5] gives b.p. 189-190° (750 mm), n_D^{20} 1.4640 and d_4^{20} 0.8646 [5].

The experiments were carried out in a flow apparatus [6] at 450° and 20 atm in presence of 0.5% Pt - Al₂O₃, 0.5% Pt - ZrO₂, and also pure Al₂O₃ and ZrO₂. Bicyclopentyl was passed at a space velocity of 0.5 hour⁻¹ at a hydrogen:hydrocarbon molar ratio of 4:1. The catalyzates were fractionally distilled through a column of 40-plate efficiency. The fractions were characterized by their physical constants, and their compositions were determined by chemical methods and by the determination of Raman spectra. The gas was analyzed in a VTI apparatus. The properties of the catalyzates and the composition of the gas are shown in Table 1.

Chilling of the catalyzate resulted in the isolation of 14 g of naphthalene, b.p. 217-218.2° (748 mm) and m.p. 79.5-80°.

TABLE 1

Properties of Catalyzates obtained in the Transformations of Bicyclopentyl at 450° in presence of Hydrogen at 20 atm

Expt. no.	Catalyst	Yield of catalyzate (% by weight)	Prop. of catalyzate		Composition of gas	
			n_D^{20}	d_4^{20}	H ₂	C _n H _{2n+2}
1	0,5% Pt — Al ₂ O ₃	87,8	1,5020	0,9067	99,6	0,4
2	0,5% Pt — ZrO ₂	93,6	1,4808	0,8732	99,3	0,7
3	Al ₂ O ₃	97,6	1,4675	0,8730	—	—
4	ZrO ₂	98,4	1,4649	0,8678	—	—

The fractional compositions of the catalyzates are given in Tables 2 and 3.

TABLE 2

Properties and Compositions of Fractions Isolated from the Catalyzate obtained in presence of 0.5% Pt — Al₂O₃

Expt. no.	Boiling point (°C at 758 mm)	n_D^{20}	d_4^{20}	Yield (% by weight on catalyzate)	Composition of fraction
1	146,4—184	1,4272	0,7672	4,0	Paraffins
2	184—187	1,4823	0,8974	9,0	Bicyclopentyl, trans-decahydronaphthalene, bicyclopentyl
3	187—198	1,4774	0,8822	6,7	cis-decahydronaphthalene, bicyclopentyl
4	198—203,6	1,5247	0,9216	2,0	—
5	203,6—204,5	1,5400	0,9666	8,2	1,2,3,4-tetrahydronaphthalene
	Residue, b.p. 207—213° (757 mm)	1,5650	0,9929	5,0	—

By chilling of the catalyzate we obtained 60.2 g of naphthalene, b.p. 217—218° (755 mm), m.p. 80°.

TABLE 3

Properties and Compositions of Fractions isolated from the Catalyzate obtained in presence of 0.5% Pt — ZrO₂

Expt. no.	Boiling point (°C at 19 mm)	n_D^{20}	d_4^{20}	Yield (% by weight on catalyzate)	Composition of fraction
1	73—76	1,4620	0,8567	1,7	Bicyclopentyl, trans-decahydronaphthalene Bicyclopentyl Bicyclopentyl, cis-decahydronaphthalene 1,2,3,4-tetrahydronaphthalene
2	76—78	1,4664	0,8688	13,8	
3	78—78,2	1,4650	0,8652	55,4	
4	78,2—83,3	1,4664	0,8690	5,5	
5	91,6—92	1,5280	0,9505	5,1	—
	Residue	—	—	1,2	

As will be seen from the results, the transformations of bicyclopentyl in presence of platinumized alumina consist mainly in isomerization into cis- and trans-decahydronaphthalenes with subsequent dehydrogenation into 1,2,3,4-tetrahydronaphthalene and naphthalene. Paraffins are formed only to an insignificant extent. Platinumized zirconia does not so readily bring about the isomerization of bicyclopentyl into the decahydronaphthalene condensed system and does not show activity with respect to the hydrogenolysis of the cyclopentane ring. The presence of only small amounts of products of the hydrogenolysis of bicyclopentyl when platinumized alumina is

used as catalyst prompted us to examine the effect of carriers on the character of the transformations of this hydrocarbon. With this object we investigated the transformations of bicyclopentyl in presence of pure alumina and zirconia under the same conditions. Fractionation of the catalyzates showed that they consisted essentially of unchanged bicyclopentyl. A small (2.8 g) high-boiling (above 225°) residue from the catalyzate obtained in presence of Al_2O_3 was not investigated.

SUMMARY

1. Bicyclopentyl, at 450° in presence of hydrogen at 20 atm and 0.5% Pt on Al_2O_3 or 0.5% Pt on ZrO_2 , is isomerized mainly into a mixture of cis- and trans-decahydronaphthalenes, which are subsequently dehydrogenated into 1,2,3,4-tetrahydronaphthalene and naphthalene.

2. Under the same conditions pure Al_2O_3 and ZrO_2 do not effect the isomerization of bicyclopentyl.

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TAUTOMERISM IN APROTIC MEDIA

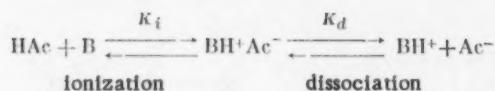
COMMUNICATION 1. PROTOLYSIS OF CARBOXYLIC ACIDS

BY TRIS (p-DIMETHYLAMINOPHENYL) METHANOL

M. I. Kabachnik and S. T. Ioffe

According to Hammett [1] it is necessary to distinguish ionization and dissociation in solutions. The ionization of the electrically neutral molecule of an acid is a protolytic reaction with the solvent resulting in the formation of the corresponding lyonium salt in the form of an ion pair; the dissociation of the latter into free (solvated) ions is the next stage and depends on the dielectric properties of the medium. According to Izmailov [2] the dissociation of acids consists of the following equilibrium reactions: solvation of the neutral acid molecule, dissociation of the solvate with formation of solvated ions, and the association of the latter into ion pairs.

Kolthoff and Bruckenstein [3] showed that, in a medium of low dielectric constant, the following equilibrium exists:

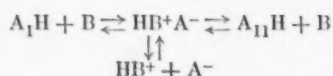


The ionization constant K_i gives a more exact expression of the strength of the acid or base than the dissociation constant K_d or the usual ionization constant K_a , which is equal to the product of the other constants ($K_a = K_i K_d$).

As one of us showed, the position of the tautomeric equilibrium of substances of an acid character ($\text{HA}_I \rightleftharpoons \text{HA}_{II}$) depends on the relative strengths of the tautomeric forms as acids in the given medium [4]. As a measure of the relative strengths we may take either the usual ionization constant K_a measured in conducting media by, e.g., the potentiometric method, or, in aprotic media, the protolysis constant K_p for the protolysis of the tautomeric forms by the proton carrier B. We have previously developed a general potentiometric method for the determination of tautomeric-equilibrium constants in conducting media [5]. For the extension of the principles of this method to aprotic media it was found to be desirable to use the indicator method and to pass from measurement of ionization constants K_a to that of protolysis constants K_p .

It is well known [6] that the indicator method is based on the ability of an indicator, used in relatively small concentrations, to adjust itself to the general buffer equilibrium. Thus, in the presence of the buffer $\text{HA} + \text{B} \rightleftharpoons [\text{HB}^+ \text{A}^-] \rightleftharpoons \text{HB}^+ + \text{A}^-$ and of the indicator $\text{HJ} + \text{B} \rightleftharpoons [\text{HB}^+ \text{J}^-]$ the ratio $[\text{J}^-] / [\text{HJ}]$ is determined by the concentration of HB^+ ions given by the buffer. Hence, the method gives a constant depending also on the dissociation constants both of the acid and of the indicator in presence of the base B.

However, the tautomeric transformation ($\text{HA}_I \rightleftharpoons \text{HA}_{II}$) is not necessarily associated with dissociation and can occur already at the protolysis stage, for it is at this stage that a common ion is formed as follows:



Hence, for the determination of the relative strengths of tautomeric acids it is better to use only one base, this being such that it can simultaneously play the parts of indicator and proton carrier. Hence, the first stage of the investigation of tautomeric equilibria in aprotic media was necessarily the study of the protolysis of non-tautomeric acids by an indicator-base in absence of a foreign buffer.

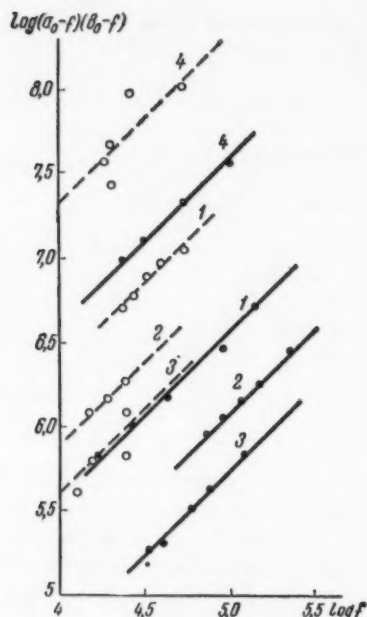
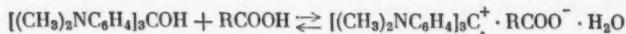


Fig. 1. Graphical determination of n and pK_p of an acid in benzene (●) and chlorobenzene (○): 1) benzoic acid; 2) acetic acid; 3) propionic acid; 4) formic acid.

way and the concentration of dye cations was then determined in the solutions to be investigated with the aid of these curves.

The protolytic reaction of the base-indicator with the acid can lead to the formation of the hydrated ion pair:



In this case the protolysis constant will be given by

$$K_p = \frac{f}{(a_0 - f)(b_0 - f)}, \quad (1)$$

in which f is the concentration of colored particles and a_0 and b_0 are the initial concentrations of acid and base respectively.

For the partial dissociation of the hydrated ion pairs the constant will be expressed as a function of some nonintegral power of f :

$$K_p = \frac{f^n}{(a_0 - f)(b_0 - f)}, \quad (2)$$

in which $1 < n < 2$, or otherwise:

$$\log(a_0 - f)(b_0 - f) = pK_p + n \log f, \quad (3)$$

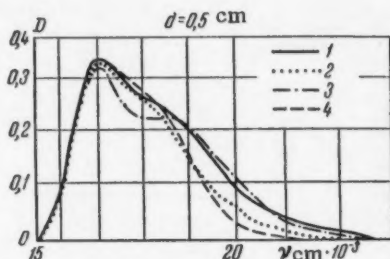


Fig. 2. Absorption spectrum of Crystal violet nitrobenzoate dissolved in 1) water, 2) chlorobenzene, 3) benzene, 4) 80% ethanol.

We decided to examine the protolytic reactions of carboxylic acids with the base of Crystal violet in media of low dielectric constant, namely benzene (dielectric constant 2.3) and chlorobenzene (dielectric constant 11). The indicator base was taken in the amount corresponding to 10-25% neutralization of the acid. The colorless 0.005 M solution of the base [7] was added to the solution of the acid. After 10-12 hours in benzene, or 2-3 hours in chlorobenzene, when the maximum intensity of color had been attained, the optical densities of the solutions were determined. By the use of a large (100-fold) excess of trichloroacetic acid graduation curves were constructed in the usual

which enables us to carry out the graphical determination of \bar{n} and pK_p from colorimetric data. In our experiments we investigated benzoic, acetic, propionic, and formic acids.

As will be seen from the graph in the coordinates $\log \frac{f}{a_0 - f}$ and $\log (a_0 - f)(b_0 - f)$ (Fig. 1), in most cases there is a good linear relationship with $\tan \alpha = 1$. Only formic acid in chlorobenzene gave a greater scatter of points, and in this case the drawing of the line is somewhat arbitrary.

The table shows the results of the calculation (by the method of least squares) of the index \bar{n} and the protolysis constant pK_p by Equation (3) from the experimental data.

TABLE
Values of \bar{n} and pK_p for Acids in Benzene and Chlorobenzene

Acid	In benzene		In chlorobenzene	
	\bar{n}	pK_p	\bar{n}	pK_p
Formic	1,08	-2,42	(1,10)	(-2,96)
Benzoic	0,95	-1,79	0,96	-2,51
Acetic	0,98	-1,24	1,00	-1,96
Propionic	1,03	-0,67	1,07	-1,27

From the above data it will be seen that in all cases the index \bar{n} is equal to unity within the limits of experimental error, and it follows that salt formation of Crystal violet base in benzene and chlorobenzene with carboxylic acids proceeds in accordance with Equation (1) with formation of a hydrated ion pair (a single particle). It should be noted here that the absorption spectrum of Crystal violet nitrobenzoate in benzene and chlorobenzene is almost identical with the absorption spectrum of this dye in conducting media, in which free ions are present (Fig. 2).

When the values of pK_p of the investigated acids in benzene and chlorobenzene are plotted on the graph it is found, in complete accord with the Bronsted equation, that the relationship is linear also in nonconducting media; the slope of the straight line is practically unity.

The authors are greatly indebted to N. A. Izmailov for discussions of the work and valuable advice and to I. V. Obreimov, in whose laboratory the absorption spectra of the solutions were determined.

SUMMARY

1. A colorimetric method was developed for the determination of protolysis constants in aprotic solvents of low dielectric constant without the use of special buffers.
2. In aprotic solvents of low dielectric constant the neutralization of an acid by a base leads to the formation of ionic pairs, which do not dissociate. The value of \bar{n} is almost unity.
3. The fact that Bronsted's relation is observed enables us to use the protolysis constants obtained in this way for the determination of equilibrium constants for tautomeric changes in nonaqueous media.

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STEREOCHEMISTRY OF NUCLEOPHILIC ADDITION AT A CARBONYL GROUP. REACTIONS OF 2-METHYLCYCLOHEXANONE

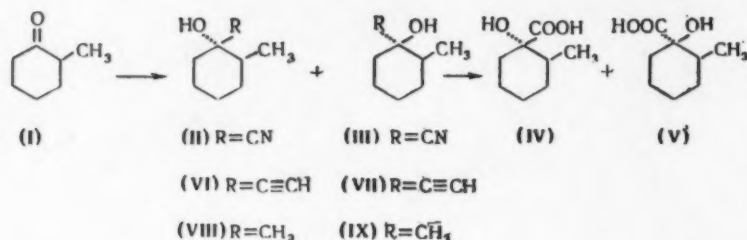
I. N. Nazarov, A. A. Akhrem, and A. V. Kamernitskii

In connection with our investigations on the introduction of oxidized side chains into cyclic compounds [1], great interest is presented by the study of the stereochemistry of the cyanohydrin and acetylene syntheses and of the Grignard reaction in this series. As an object for investigation we selected 2-methylcyclohexanone (I), which can form two geometric isomers of tertiary alcohols by addition at the carbonyl group*.

In the literature there is scarcely any reference to the possibility of the occurrence of stereospecific reactions with ketones of this sort, if we leave their reduction with metals or complex metal hydrides out of consideration [2]. In the condensation of the ketone (I) with acetylene in liquid ammonia there is formed a mixture of acetylenic alcohols with a predominance of the liquid isomer [3], the configuration of which has not been established. Reaction of methylmagnesium iodide with ethyl 4-oxocyclohexanecarboxylate proceeds selectively with formation of ethyl trans-4-hydroxy-4-methylcyclohexane-carboxylate [4], and reaction of methylmagnesium iodide with 2-chlorocyclohexanone gives trans-2-chloro-1-methylcyclohexanol [5]. However, in the reduction of the ketone (I) with sodium [6] or with complex metal hydrides [7], the entering substituent (in this case hydrogen) takes up predominantly the cis position with respect to the substituent already present.

EXPERIMENTAL

We carried out the hydrolysis of the previously described [8] mixture of cis- and trans-1-hydroxy-2-methylcyclohexanecarbonitriles (II + III) with acetic and hydrochloric acids, and the resulting mixture of cis- and



trans-1-hydroxy-2-methylcyclohexanecarboxylic acids* • (IV), m.p. 110.5–111°, and (V), m.p. 94.5–95°) was resolved by chromatography on alumina. In this way it was shown that the ratio of the amounts of cis- and trans-1-hydroxy-2-methylcyclohexanecarbonitriles ((II), m.p. 53–54°, and (III), a liquid) formed in the reaction of the ketone (I) with acetone cyanohydrin is 4 : 1.

* The configuration will be named always according to the entering substituent.

•• The configurations of the products were proved by referring them to the known [9] pair of isomers, cis- and trans-1-2-dimethylcyclohexanols. A detailed description of the experiments will be published later.

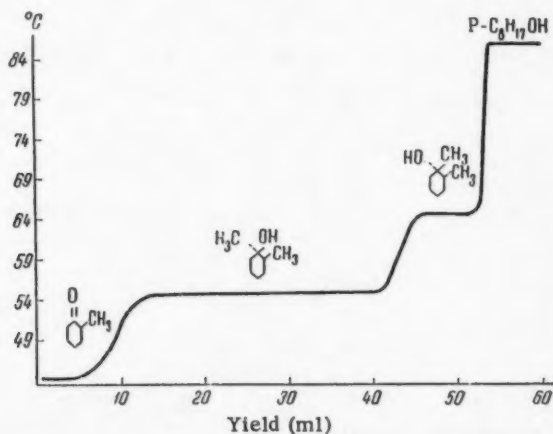
TABLE
Steric Orientation in Nucleophilic-addition Reactions at the Carbonyl
Group of 2-Methylcyclohexanone

Reagent	Entering substituent	Composition of mixture obtained (%)		Literature reference
		cis form	trans form	
Na in alcohol	H	97-99	1-3	[6]
$(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$	$\text{C} \equiv \text{N}$	80	20	—
LiAlH_4	H	64	36	[7]
$\text{CH} \equiv \text{CH}$	$\text{C} \equiv \text{CH}$	60	40	—
CH_3MgI	CH_3	25	75	—

Condensation of the ketone (I) with acetylene under a pressure of 7 atm in dry ether with an addition of ethanol in presence of potassium hydroxide powder (10 hours) gave a mixture of cis- and trans-1-ethynyl-2-methylcyclohexanols (VI) and (VII) in 86% yield, and by chilling this mixture we isolated the cis alcohol (VI), m.p. 56-57°. By further separation of the mixture it was shown that the ratio of the amounts of cis- and trans-1-ethynyl-2-methylcyclohexanols (VI) and (VII) was 3 : 2. By oxidation of the cis alcohol (VI) with potassium permanganate we obtained the cis hydroxy acid (IV), m.p. 110.5-111°, and by oxidation of the trans alcohol (VII), a liquid) we obtained the trans hydroxy acid (V), m.p. 94.5-95°. It was shown, therefore, that cyano-hydrin and acetylene syntheses with 2-methylcyclohexanone (I) are sterically selective with predominance in the mixture of products of cis addition at the carbonyl group.

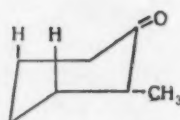
For comparison purposes the Grignard reaction was carried out between methylmagnesium iodide and the ketone (I) under the usual conditions. This resulted in a 92% yield of a mixture of cis- and trans-1,2-dimethylcyclohexanols (VIII) and (IX), having b.p. 56-61° (11 mm) and n_D^{20} 1.4608. From 45 ml of this mixture with an addition of 10 ml of the original ketone (I) and 15 ml of high-boiling octyl alcohol, fractionation through a column of 35-plate efficiency yielded 7 ml of cis-1,2-dimethylcyclohexanol (VIII) (b.p. 74.5° (15.5 mm), n_D^{20} 1.4645, and m.p. 22-23°) and 24 ml of trans-1,2-dimethylcyclohexanol (IX) (b.p. 61° (13 mm), n_D^{20} 1.4619, and m.p. 11-13°) [9]. The fractionation curve (see figure) shows that in this case the ratio of the amounts of cis and trans alcohols (VIII) and (IX) was 1 : 3.

We showed, therefore, that reaction between 2-methylcyclohexanone (I) and methylmagnesium iodide is also sterically selective, but the selectivity is reversed in sense with respect to the case of the cyano-hydrin and acetylene syntheses and the reduction of the keto group (see table).



A similar position is found in the series of 17 α -oxo-D-homosteroids (X), for which it has been shown [10] that reaction with methylmagnesium halides leads exclusively to 17 α - α -hydroxy-D-homosteroids, whereas in the reduction of the ketones (X) with sodium borohydride [11], and in the acetylene synthesis [12], 17 α - β -hydroxy-D-homosteroids are mainly formed.

It may be supposed that the opposite sense of the selectivity of the Grignard reaction in the case of cyclohexanones as compared with the cyanohydrin and acetylene syntheses, is to be explained by the greater sensitivity of this reaction to the steric hindrance set up by axial hydrogen atoms in the 3-position with respect to the keto group.



SUMMARY

1. A study was made of the stereochemistry of the addition reactions of hydrogen cyanide, acetylene, and methylmagnesium iodide with the carbonyl group of 2-methylcyclohexanone.
2. Differing relative amounts of *cis* and *trans* isomers are obtained in these reactions.

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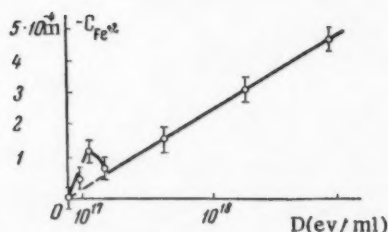
* Original Russian pagination. See C.B. translation.

RADIATION-INDUCED OXIDATION OF FERROUS IRON IN AQUEOUS SOLUTIONS

B. V. Ershler and V. G. Firsov

In previous investigations [1-4] an unexpected increase was found in the rate of oxidation of ferrous iron under the action of γ -rays in presence of dissolved oxygen with increase in the concentrations of Fe^{2+} and acid (H_2SO_4 , HCl , H_3PO_4). The limiting rate of oxidation was 63 g-equiv. per 100 ev of absorbed energy and was attained in 12 millimolar ferrous ammonium sulfate at an acid concentration of more than 4 N. In an oxygen-free medium the rate of oxidation did not increase so markedly, attaining 7.5 g-equiv. per 100 ev. The results were explained by the participation of activated water molecules capable of transferring energy to dissolved oxygen bound in a complex with ferrous ions.

If it is supposed that dissolved oxygen takes part in the reaction, it would be expected that increase in the oxygen pressure during the time of irradiation would increase the rate of oxidation, whereas no such effect is observed [2]. The effect of the acid concentration also cannot be explained by the direct participation of activated molecules. The value found for the rate of oxidation of Fe^{2+} in 0.8 N H_2SO_4 (about 4) is also unusual; in several investigations a value of about 8 has been found. Determinations by several authors [5-7] of the relation of yield of Fe^{3+} ions to acidity, carried out by spectrophotometric analysis, showed that the yield of ferric iron is independent of iron concentration (1-18 millimolar) and acid concentration (up to 5 N). The work of these investigators raised doubts concerning the existence of this effect of increased rate of oxidation of ferrous iron, although it was detected when a different method of measuring the extent of chemical change in the solution was used (determination of the loss of Fe^{2+}) [8]. All these facts made it extremely desirable to carry out a series of experiments in order to determine under what precise conditions this effect arises.



Oxidation of Fe^{2+} at an irradiation intensity of 15.3 roentgens/second

In the present paper we present more detailed data on the relation of the rate of oxidation of ferrous iron in presence of dissolved oxygen to the time of contact of the solutions with oxygen and the intensity of the radiation. It was found that at low dosage (not greater than 15 roentgens/second) the magnitude of the effect in solutions subjected to preliminary saturation with oxygen is apparently more than can be accounted for by contamination and titration errors, but is nevertheless extremely small and poorly reproducible. It should be noted that the effect was followed up to 1-2% oxidation of the total amount of Fe^{2+} , the experimental accuracy was not high, and the G-value for the enhanced rate of oxidation was determined with a possible error of 30-40%.

In freshly prepared solutions the effect is absent. In view of this, all experiments in the present work were carried out with solutions that had been kept for some time in an oxygen atmosphere before irradiation. The results of one of the series of experiments are represented graphically in the figure. A solution of ferrous ammonium sulfate in sulfuric acid (4 N) was kept under oxygen at 1-2 atm for 170 hours. Curve 1 corresponds to the oxidation of Fe^{2+} with $G = 15.5$, and Curve 2 was obtained experimentally, the initial yield being $G = 58-112$ g-equiv./100 ev. As will be seen, Curve 2 has a maximum, and beyond this it merges with Curve 1 and oxidation proceeds in the usual way.

Attempts to detect the effect at high intensities of radiation (up to 350 roentgens/second) were unsuccessful. Change in the concentration of Fe^{2+} (1.0-22.6 millimolar), the concentration of H_2SO_4 (up to 5.13 N), the intensity of irradiation (120-350 roentgens/second), oxygen pressure (to 8-11 atm), and the duration of the preliminary maintenance of the solution under oxygen (pressure 1 atm and 0.2 atm) (up to 75 hours) resulted in a rate of oxidation of iron in the initial section of $G = 15.5$ g-equiv./100 ev. It was found at the same time that the rate of oxidation in the part of the curve in which oxygen was fully consumed was $G = 7.9 \pm 0.4$. The ratio of rates is 1.97 ± 0.09 , which is in close agreement with the results of other investigators [9-12]. It should be noted that in these experiments a rate of oxidation of Fe^{2+} of $G = 4$ was not observed.

The magnitude of the effect of enhanced oxidation (duration along the axis of abscissae) depends, according to our results, on the duration of the preliminary contact of the solutions with oxygen or air. Hence, under the action of sufficiently intense γ -radiation (from 1 to about 15 roentgens/second) the enhanced-oxidation effect is not very stable and can be observed only when the solution has been saturated with oxygen for a long time.

Under the action of ultraviolet radiation the oxidation of Fe^{2+} proceeds at a rate that depends on the acid concentration in the solution [13]; the character of the oxidation curves is similar to that of the curves described above. It may be considered that the small, poorly reproducible effect produced by γ -rays of low intensity is due to some admixture of ultraviolet radiation. Also, it is possible that γ -radiation brings about the decomposition of the complex (with return of O_2 and ferrous ions to the solution, which causes the fall in Curve 2 and absence of the effect at high intensities), whereas ultraviolet radiation does not have such an influence.

SUMMARY

An investigation was made of the dependence of the yield G in the oxidation of aqueous solutions of ferrous iron on various factors. The limits within which the enhanced- G effect is observed and the accuracy with which the effect can be measured were established.

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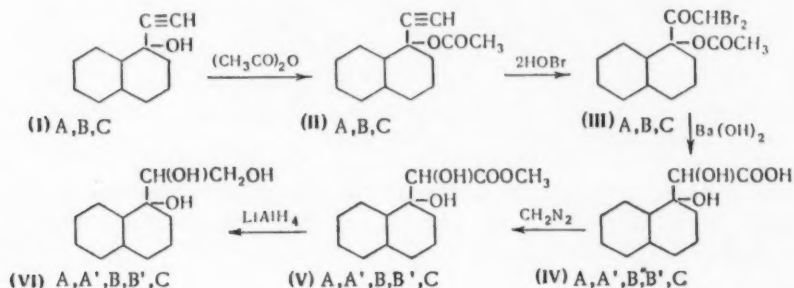
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INTRODUCTION OF HYDROXYACETONE, GLYCEROL, AND
DIHYDROXY-CARBOXYLIC SIDE CHAINS INTO *cis*- AND
trans-DECAHYDRONAPHTHALENE DERIVATIVES

I. N. Nazarov, G. V. Aleksandrova, and A. A. Akhrem

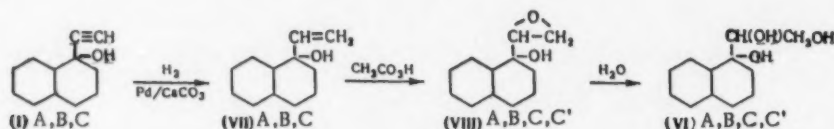
This paper is devoted to the study of the conversion of *trans*-1-ethynyldecahydro-1-naphthols (I) A and (I) B, *cis*-1-ethynyldecahydro-1-naphthol (I) C, and the acetic esters (II) A, B, and C of these alcohols [1] into compounds having hydroxyacetone, glycerol, and dihydroxy-carboxylic side chains characteristic of corticosteroids by means of the dibromo-ketol and glycidol methods that we developed previously [2]; we report also an investigation of the stereochemistry of the products.

The dibromo-ketol method for the preparation of compounds with dihydroxy-carboxylic and glycerol side chains consists in the addition of two molecules of hypobromous acid to acetic esters of acetylenic alcohols (II) [2] with formation of acetic esters of 1-(dibromoacetyl)-decahydro-1-naphthols (III), which undergo an intramolecular rearrangement similar to the Favorskii rearrangement [2,4] when treated with barium hydroxide, the products being decahydro-1-hydroxy-1-naphthaleneglycolic acids (IV).



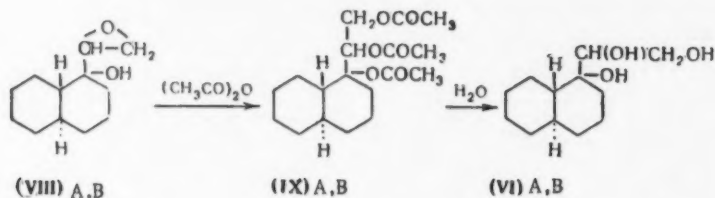
By reduction with lithium aluminum hydride, the methyl esters of these acids (V) are converted into 1-(decahydro-1-hydroxy-1-naphthyl)-1,2-ethanediols (VI). The rearrangement of the acetic esters of dibromo ketols of the *trans*-decahydronaphthalene series (III) A and (III) B during hydrolysis is not stereospecific and proceeds in both possible directions, giving in each case two individual dihydroxy acids: (IV) A, m.p. 190-191°, (IV) A', m.p. 164-165°, (IV) B, m.p. 138-139°, and (IV) B', m.p. 175-175.5°. Unlike the hydrolysis of dibromo ketols of the *trans* series, the hydrolysis of the dibromo ketol of the *cis*-decahydronaphthalene series (III) C with barium hydroxide proceeds in a sterically selective manner with formation of only one isomer: *cis*-decahydro-1-hydroxy-1-naphthaleneglycolic acid (IV) B, m.p. 155-156°. The methyl esters (V), were prepared in quantitative yield by treatment of the dihydroxy acids (IV) with ethereal diazomethane. In this way we synthesized five of the six theoretically possible stereoisomers of *cis*- and *trans*-decahydro-1-hydroxy-1-naphthaleneglycolic acids (IV). By reduction of their methyl esters with lithium aluminum hydride we obtained five stereoisomeric 1-(decahydro-1-hydroxy-1-naphthyl)-1,2-ethanediols: (VI) A, m.p. 117-118°, (VI) A', m.p. 119-120°, (VI) B, m.p. 92-93°, (VI) B', m.p. 158-159°, and (VI) C, m.p. 109-110°.

The glycidol method of introducing a glycerol side chain consists in the hydrogenation of 1-ethynyldecahydro-1-naphthols (I) into decahydro-1-vinyl-1-naphthols (VII) [5], oxidation of these into 1-(epoxyethyl) decahydro-1-naphthols (VIII), and hydrolysis with formation of the above described 1-(decahydro-1-hydroxy-1-naphthyl)-1,2-ethanediols (VI):

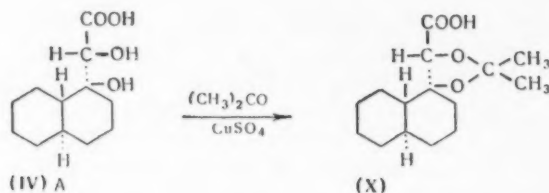


Oxidation of the ethylenic alcohols of the trans-decahydronaphthalene series (VII) A and (VII) B with peroxyacetic acid in chloroform proceeds in a sterically selective manner and leads in each case to a single glycidol, (VIII) A, m.p. 116-117°, and (VIII) B, m.p. 112-114°, respectively, whereas the oxidation of the ethylenic alcohol of the cis-decahydronaphthalene series (VII) C is not stereospecific and gives both possible stereoisomeric glycidols in the ratio 1 : 1 (VIII) C, m.p. 100-101°, and (VIII) C', m.p. 90-91°. By the action of dilute acetic acid on the glycidols (VIII) we obtained the above-described triols (VI) A, (VI) B, and (VI) C together with the cis triol (VI) C', m.p. 115-117°. Hence, by the use of the dibromo-ketol and glycidol methods we succeeded in synthesizing all six theoretically possible isomers of cis- and trans-1-(decahydro-1-hydroxy-1-naphthyl)-1,2-ethanediols (VI) corresponding to 1-ethynyldecahydro-1-naphthol (I).

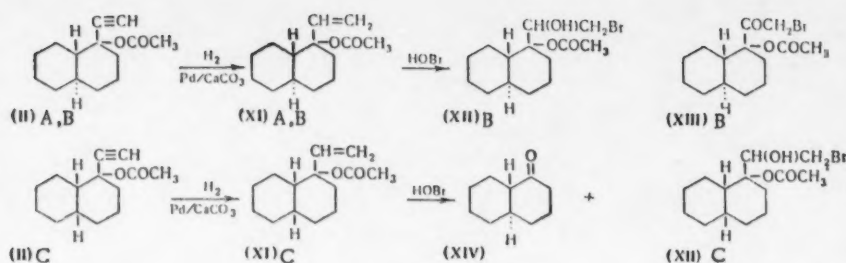
Boiling of the trans glycidols (VIII) A and (VIII) B with excess of acetic anhydride [6] gave the triacetates (IX) A, b.p. 140-144° (1 mm) and n_D^{25} 1.4782, and (IX) B, the hydrolysis of which with a solution of potassium carbonate in aqueous methanol again led to the formation of the above-described triols (VI) A and (VI) B:



With the object of determining the configurations of the hydroxyls in the side chain, we attempted to prepare the "acetates" [7] of the decahydro-1-hydroxy-1-naphthaleneglycolic acids. Only from the acid (IV) A, m.p. 190-191°, did we succeed in preparing an acetate (X), m.p. 124-125°, which probably indicates the close spatial disposition of the hydroxyls in this acid.



In the study of the addition of hypobromous acid to the decahydro-1-vinyl-1-naphthol acetates (XI) A, b.p. 100-102° (3 mm) and $n_D^{16.5}$ 1.4815, (XI) B, b.p. 102-104° (3 mm) and $n_D^{16.5}$ 1.4882, and (XI) C, b.p. 97-99° (1 mm) and n_D^{20} 1.4862, it was found that the three isomers behave differently in this reaction.



The acetic ester (XI) B combines smoothly with one molecule of hypobromous acid and forms the crystalline acetic ester of the bromohydrin (XII) B, m.p. 140-141°, whereas the acetic ester (XI) A, treated under these conditions, gives an oil which decomposes in vacuum distillation. In the reaction of decahydro-1-vinyl-1-naphthol acetate (XI) C with hypobromous acid, the main product isolated was trans-octahydro-1-(2H)-naphthalenone (XIV), and only a small amount was obtained of a crystalline substance, m.p. 137-139°, which was close in analysis to the bromohydrin acetic ester (XII) C. Numerous attempts to oxidize the bromohydrin (XII) B into the corresponding α -bromo ketol (XIII) B and to replace bromine by the hydroxy or acetoxy group were not successful: in all cases the bromohydrin (XII) B was recovered unchanged.

The previously noted [1] high steric hindrance of the side chain in trans-1-ethynyldecahydro-1-naphthol (I) B, as compared with the acetylenic alcohol (I) A, in, for example, hydration reactions found further confirmation in the present work. This was manifested in the greater difficulty found in the hydrolysis of the dibromo ketol (III) B, in the nonformation of the acetates of the dihydroxy acids (IV) B and (IV) B', in the poorer results obtained in the oxidation of the ethylenic alcohol (VII) B into the glycidol (VIII) B, and finally in the impossibility of bringing about the oxidation of the hydroxy group in the bromohydrin (XII) B and the replacement of its bromine atom by the hydroxy or acetoxy group.

SUMMARY

1. A study was made of the dibromo-ketol and glycidol methods of introducing glycerol and dihydroxycarboxylic side chains into the molecules of cis- and trans-decahydro-1-naphthols.
2. Six stereoisomers of cis- and trans-1-(decahydro-1-hydroxy-1-naphthyl)-1,2-ethanediols (VI), four isomeric 1-(epoxyethyl) decahydro-1-naphthols (VIII), and five stereoisomeric decahydro-1-hydroxy-1-naphthalenecarboxylic acids (IV) were isolated.

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HETEROCHAIN POLYESTERS

COMMUNICATION 12. TEREPHTHALIC AND ISOPHTHALIC POLYESTERS OF DIHYDRIC PHENOLS*

V. V. Korshak and S. V. Vinogradova

With the object of studying the effect of the structures of the reactants on the physical properties of the polyesters obtained from them, we synthesized and investigated terephthalic and isophthalic polyesters of dihydric phenols of various structures. The table gives data on these polyesters. All the polyesters, except the *o, o'*-biphenol polyesters, were prepared by polycondensation in biphenyl solution in a stream of nitrogen with gradual rise of temperature from 120° to 230°. The polyesters of *o, o'*-biphenol were synthesized in the melt. The reactants used in the preparation of the polyesters were the acid chlorides of terephthalic and isophthalic acids and the various diols.

As will be seen from the table, the softening temperature of the polyester depends greatly on the structure of the polymer chain. The highest softening temperature is possessed by the terephthalic polyester of hydroquinone, which does not melt in a capillary below 500°, but merely becomes cream in color at high temperatures. The thermomechanical curve of this sample shows that this polyester does not undergo deformation below 360°, i.e. the glass and softening points lie at still higher temperatures. The isophthalic ester of hydroquinone has a lower but still very high softening temperature. The thermomechanical curve of this polymer shows that deformation starts at about 350°.

The softening point of a polyester depends also on the mutual disposition of the functional groups in the diol. Thus, the resorcinol polyesters of terephthalic and isophthalic acids have much lower softening points than the corresponding hydroquinone polyesters. Hence, in the case of polyesters in which the chain is made up only of aromatic units and ester groupings we observe the same regularities as in the case of the polyesters derived from aromatic dicarboxylic acids and aliphatic glycols. The polyesters from acids and diols having their functional groups in the para positions have higher softening points than polyesters derived from reactants in which the functional groups are in the meta position. It is characteristic of resorcinol polyesters that they remain transparent after fusion in a capillary.

We synthesized also the terephthalic and isophthalic polyesters of 4,4'-isopropylidenediphenol. The softening points of these polyesters, determined in a capillary, were 350° and 275° respectively. The glass points were 200° for the isophthalic polyester and above 300° for the terephthalic polyester. The crystallinities of these polyesters were low (only about 10%), i.e. they were almost amorphous. The terephthalic and isophthalic polyesters of *p, p'*-(*p*-phenylenebis(diphenylmethylene)) diphenol were powders which remained transparent after fusion in a capillary. The glass point of the first polyester was about 200°, and that of the second was about 120°. The *p, p'*-(*p*-phenylenebis(diphenylmethylene)) diphenol polyesters had much lower softening points than the 4,4'-isopropylidenediphenol polyesters, in spite of the presence of a large number of aromatic nuclei in its molecule. This is probably associated with the greater disturbance of the density of packing of the polymer chains resulting from the large number of bulky phenyl groups.

Naphthalenediol polyesters have very high softening points. Thus, the 1,6- and 1,5-naphthalenediol

*Laboratory workers V. S. Artemova and D. T. Morozova took part in the experimental work.

**See pp. 620 and 621.

polyesters could not be melted without decomposition. In order to determine the effect of the presence of an aromatic nucleus in the diol on the softening point of the polyester it is desirable to compare a series of polyesters. Such a series is made up of the terephthalic polyesters of hydroquinone (softening point above 500°), trans-1,4-cyclohexanediol (312°), cis-1,4-cyclohexanediol (205°), o-xylene- α, α' -diol (95°), and 1,4-butanediol (222°). Comparison shows that for a given number of carbon atoms between the hydroxy groups of the diol the softening point of the terephthalic polyester depends greatly on the structure of the diol. The diols can be arranged in the following order of diminishing softening point of the polyester: hydroquinone > trans-1,4-cyclohexanediol > 1,4-butanediol > cis-1,4-cyclohexanediol > o-xylene- α, α' -diol. The softening point is lowered to the greatest extent in the case of aromatic diols having their functional groups in the ortho position and separated from the aromatic nucleus by a methylene group. Moreover, in contrast to the opaque polyesters of hydroquinone, trans-1,4-cyclohexanediol, and 1,4-butanediol, the o-xylene- α, α' -diol polyester is a transparent amorphous substance.

As will be seen from the table, the terephthalic and isophthalic polyesters of aromatic diols are extremely sparingly soluble in benzene, dichloroethane, and cresol. From some of the polyesters, e.g. the 4,4'-isopropylidene polyesters, we prepared transparent, somewhat colored films from the melt in an atmosphere of nitrogen. Mechanical tests showed that these films had a very low extensibility (3-8%), which did not increase greatly with rise in temperature. However, the tensile strength of these films at room temperature was fair (620 kg/sq. cm).

In conclusion the authors express their thanks to workers in the laboratories directed by G. L. Slonimskii and A. I. Kitaigorodskii for the performance of mechanical and x-ray investigations on the polymers, and also to E. S. Krongaus for placing some p'-(p-phenylenebis(diphenylmethylene)) diphenol at our disposal.

SUMMARY

1. Terephthalic and isophthalic polyesters of dihydric phenols were synthesized.
2. The effect of the structures of the reactants on the properties of the polyester were discussed.

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TABLE

Structural unit of polyester	Softening point of polyester (°C)	Solubility (g/liter) in benzene	Solubility (g/liter) in dichloroethane	η_{sp} of solution of polyester	Crystallinity (%)	Appearance of polyester
	Does not melt below 500°	0	0	Does not dissolve in cresol	>90	White powder
	~320*	0	0,7	Ditto	~90	„ „ „
	270—285	—	0,7	„ „	~70	White powder. After fusion in capillary remains transparent.
	230—245**	0,6	1,1	„ „	<50	Ditto
	172—175	—	—	0,11	0	Hard, transparent, brown. Gives long filaments from melt
	158—160	—	—	0,11	Ditto	Ditto
	about 350 with darkening	0,6	1,4	Dissolves in- completely	~10	White powder. After fusion in capillary remains transparent.

TABLE (Cont'd).

	275—285	—	2,1****	0,25***	~10	Ditto
	220—245	—	0,4	Does not dissolve	~20	„
	157—170	—	—	0,07	0	Cream powder. After fusion in capillary it remains transparent
	230—265	—	—	0,05		Pale-yellow powder. After fusion in capillary it remains transparent
	188—210	—	—	0,07		Ditto
	Does not melt below 500° ****	—	—	—		Yellow powder

• It was difficult to determine the softening point exactly because the polymer darkened considerably at 300°.

•• It melted at 230–245°, but the melt was extremely thick, which was generally true of other polyesters in the table.

••• The molecular weight of the polyester of specific viscosity 0.195, determined by the isopiestic method, was 29,000.

•••• The solubility was determined on a sample of specific viscosity 0.195.

••••• At about 300° the polymer began to sinter somewhat, and at 350° it began to darken; the darkening increased with rise in temperature; at 500° the polymer was black.

SELECTIVITY OF CATALYSTS

COMMUNICATION 2. REDUCTION OF MESITYL OXIDE OVER COPPER AND ZINC-COPPER CATALYSTS

L. Kh. Freidlin, A. S. Sultanov, and M. F. Abidova

We have shown previously [1] that zinc has the rare property of catalyzing the reduction at atmospheric pressure of the C=O bond without affecting the C=C bond. It is accordingly found that the reduction of allyl alcohol over this catalyst does not proceed directly, but with intermediate formation of propionaldehyde [2]. In this reaction a zinc-copper catalyst behaves similarly. It may be supposed, therefore, that, like the zinc catalyst, it will selectively hydrogenate a carbonyl bond in presence of an ethylenic bond.

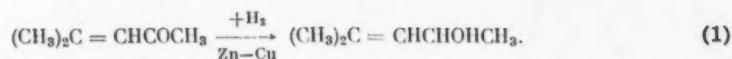
In view of this we have now investigated the reduction of mesityl oxide over a zinc-copper catalyst, which was prepared by the leaching of a 50: 33: 17 Al-Cu-Zn alloy and subsequent washing with water. The reaction was carried out under flow conditions. The experimental procedure and method of preparing the catalyst are described in greater detail in [1]. The catalyzate was analyzed for the content of carbonyl compounds (oxime method) and for the content of unsaturated compounds (from the consumption of hydrogen in the hydrogenation of a sample of the product in presence of Raney nickel in 96% ethanol at 20°). Under these conditions the carbonyl group was not reduced.

TABLE 1

Ex- per- iment	Tempera- ture(°C)	Content (%) in catalyzate of		Composition of catalyzate (%)			
		ketones •	unsaturated compounds•	mesityl oxide	4-Methyl-3- penten-2-ol	4-Methyl- -2-pentanone	4-Methyl-2- -pentanol
1	75	40,0	100,0	39	58	0	0
2	87	19,2	100,0	19	78	0	0
3	100	16,5	100,0	16	80	0	0
4	125	23,0	93,0	15	73	7	0
5	150	37,4	79,0	16	60	20	0
6	175	50,0	7,0	0	7	48	41

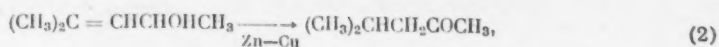
• Calculated on the amount of mesityl oxide.

As will be seen from Table 1 and Fig. 1, at 75-100° the degree of unsaturation of the catalyzate does not change, and only the carbonyl group is hydrogenated:

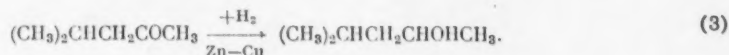


Above 100° the content of unsaturated compounds in the catalyzate begins to diminish and the content of carbonyl compounds to increase. Hence, as in the case of a zinc catalyst, in presence of a zinc-copper catalyst with

rise of temperature the 4-methyl-3-penten-2-ol formed is isomerized into a saturated ketone:



which appears to be reduced further into 4-methyl-2-pentanol:



From the analytical data obtained we made a tentative calculation of the compositions of the catalyzates obtained at various temperatures. Examples of such calculations are given in [1]. The figures given in Table 1 are somewhat lower than the calculated ones, because they have been recalculated as percentages on the amounts of mesityl oxide passed. Comparing the data in Table 1 with those given in [1] we see that the isomerization (Equation (2)) occurs with much more difficulty over a zinc-copper catalyst than over a zinc catalyst.

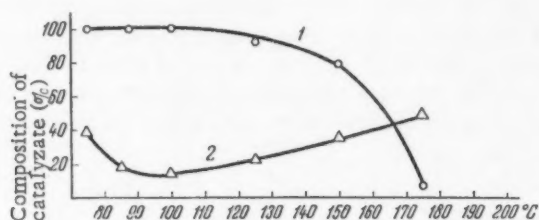


Fig. 1. Reduction of mesityl oxide at various temperatures over a zinc-copper catalyst: content in the catalyzate of 1) unsaturated compounds, 2) ketones.

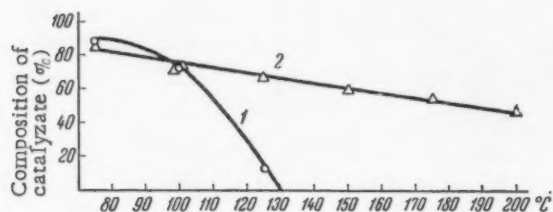


Fig. 2. Reduction of mesityl oxide at various temperatures over a copper catalyst: content in the catalyzate of 1) unsaturated compounds, 2) ketones.

It is known that copper is able to catalyze the reduction at atmospheric pressure both of aldehydes and ketones and also of unsaturated compounds. The selectivity that we have shown to be possessed by a zinc-copper catalyst is therefore due to its zinc component. In order to verify this view we studied also the relative rates of hydrogenation of the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bonds of mesityl oxide over a copper catalyst. The catalyst was prepared by the leaching of a 33 : 67 Cu - Al alloy by the procedure used in the preparation of the zinc-copper catalyst. From Table 2 and Fig. 2 it follows that the copper and zinc-copper catalysts differ greatly in behavior. The composition of the catalyzate, as calculated from the analytical data, shows that in presence of the copper catalyst the unsaturated alcohol is scarcely formed at all; the sole reaction products are 4-methyl-2-pentanone and 4-methyl-2-pentanol. In the experiments at 75° and 100° the reductions in the amounts of unsaturateds and ketones in the catalyzate were small and about equal. At 125° only about 13% of unsaturateds remained in the catalyzate, and at 150° they were completely absent. On the other hand, the content of carbonyl compounds diminished slowly, and at 200° it was still 48.4%. Hence, over a copper catalyst hydrogen adds primarily at the $\text{C}=\text{C}$ bond.

TABLE 2

Ex- peri- ment	Tempera- ture(°C)	Content (%) in catal- yzate of		Composition of catalyzate (%)			
		ketones*	unsaturated compounds*	mesityl oxide	4-Methyl-3- penten-2-ol	4-Methyl-3- pentanone	4-Methyl-2- pentanol
1	75	84,8	88,5	83	4	0	11
2	100	71,0	71,5	68	4	0	22
3	125	65,7	13,0	12	0	50	33
4	150	60,0	0,0	0	0	58	38
5	175	55,0	0	0	0	52	43
6	200	48,4	0	0	0	46	49

* Calculated on the amount of mesityl oxide.

For final confirmation of this conclusion it was necessary to verify whether the unsaturated alcohol, if formed intermediately, would not be isomerized very rapidly into 4-methyl-2-pentanone over a copper catalyst. The experiment carried out for this purpose showed that in the passage of 4-methyl-3-penten-2-ol (containing 4.1% of mesityl oxide) at 125° at the usual rate only 5.7% of carbonyl compounds was formed in the catalyzate. Hence, in contrast to the behavior over a zinc-copper catalyst, in presence of a copper catalyst 4-methyl-2-pentanone is formed not through the unsaturated alcohol and its isomerization, but by addition of hydrogen at the C=C bond.

SUMMARY

1. A zinc-copper catalyst selectively catalyzes the hydrogenation of the C=O bond in mesityl oxide, while remaining inert for the hydrogenation of the C=C bond. On the other hand, over a copper catalyst hydrogen adds primarily at the C=C bond. Over a copper catalyst 4-methyl-3-penten-2-ol is not isomerized at 125°.
2. The selectivity of a zinc-copper catalyst is determined by its zinc component, and its lower activity, as compared with a zinc catalyst, for the isomerization of the unsaturated alcohol into the saturated ketone is due to the presence of copper in the catalyst.

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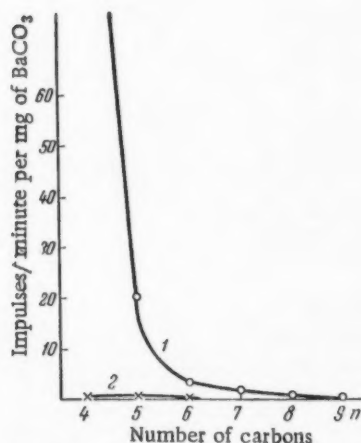
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TRANSFORMATIONS OF BUTENE UNDER THE CONDITIONS OF SYNTHESIS FROM CO AND H₂ OVER FUSED IRON CATALYSTS

Iu. B. Kriukov, A. N. Bashkistrov, V. K. Butugin, L. G. Liberov,
and N. D. Stepanova

It is known that olefins, by reaction with CO and H₂ or under the influence of these substances, can undergo various reactions, namely hydrocondensation [1,2], hydropolymerization [3], and hydroformylation ("oxo synthesis") [4,5]. The addition of olefins to the original gas under the conditions for the synthesis of hydrocarbons results in an increase in yield of hydrocarbons of molecular weight higher than that of the added olefin [6, 7]. This can be explained either by the participation of olefins in the synthesis process or by the displacement of the equilibrium between synthesis products on the catalyst surface. With the aid of radioactive ethylene it was shown that on a cobalt catalyst ethylene can act as an initiator for the growth of carbon chains in the synthesis of hydrocarbons from CO and H₂ [8].



Dependence on number of carbons of the specific activity of 1) hydrocarbons and 2) alcohols.

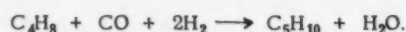
These facts have suggested to many investigators that olefins play an active part in the synthesis of aliphatic compounds from CO and H₂. It is supposed, in particular, that olefins may act as intermediaries in the synthesis of hydrocarbons and oxygen-containing compounds from CO and H₂ [6, 9]. It has recently been suggested also that the hydropolymerization of olefins may be the final stage in the synthesis of hydrocarbons from CO and H₂ [10].

In the present work we have attempted to determine the ways along which reaction proceeds with olefins formed in the course of the synthesis of hydrocarbons and oxygen-containing compounds from CO and H₂. As an indicator of the behavior of an olefin under the actual conditions of the synthesis we used butene labeled with C¹⁴ in position 1. The experiments were carried out with fused iron catalysts at 90 atm and 210-220°. The labeled butene was added to the synthesis gas (CO + 2H₂) in small amounts (about 0.03% by volume) that would not disturb the conditions existing on the catalyst surface.

The liquid synthesis products consisted of approximately equal amounts of hydrocarbons and oxygen-containing compounds, mainly alcohols. The hydrocarbons and alcohols were separated and then fractionated through a column. The fractions, ranging from C₁ to C₉, and the residues were subjected to radiometric analysis by the method used previously [11].

The results of the experiments are given in the table and figure. It will be seen that the butene takes practically no part in the formation of hydrocarbons higher than C₈ and of alcohols. These results indicate that butene, and probably olefins in general, is not an intermediary in the synthesis of hydrocarbons and oxygen-containing compounds from CO and H₂ over fused iron catalysts. Moreover, butene is not transformed on the surface of the iron catalyst into active intermediaries, which may participate in the general process of growth of carbon

chains or may initiate this growth process. It was found also that under the conditions studied butene can react to some extent with CO and H₂ with formation of a C₅ hydrocarbon, e.g. by the reaction:



About 8% of the C₅ hydrocarbons were formed in this way. Other olefins present in the reaction zone behave in the same way. The activity detected in hydrocarbons higher than C₄ and due to this sort of transformation gradually fades with increase in the length of the carbon chain.

The distribution of radioactivity which we found among the synthesis products indicates the occurrence of various other reactions of butene in the reaction zone. Up to 13% of the butene undergoes hydrocracking under the conditions studied; this is indicated by the activity found in methane and other lower hydrocarbons. Hydrogenation of butene into butane proceeds at an appreciable rate. It must be noted, however, that most of the butane (more than 90%) is formed not by the hydrogenation of desorbed butene, but by the hydrogenation of an intermediate surface compound. Oxidation of butene with formation of CO₂ was also detected, and in this reaction the water of reaction appears to act as oxidizing agent. The hydration of butene (formation of butanol) and the oxo synthesis (formation of pentyl alcohol) proceed only to a very slight extent.

TABLE
Distribution of Radioactivity among the Synthesis Products

Hydrocarbons	Amount (%) of radio ac- tivity intro- duced	Alcohols	Amount (%) of radio ac- tivity intro- duced
C ₁	12,40	C ₁ + C ₂	0,16
C ₂ + C ₃	0,20	C ₃	0,07
C ₄ H ₈ *	69,80	C ₄	0,02
C ₄ H ₁₀	3,80	C ₅	0,04
C ₅	3,90	C ₆	0,01
C ₆	0,34	C ₇ and higher	0,00
C ₇	0,27		
C ₈	0,14	Carbon monoxide	0,00
C ₉	0,04	Carbon dioxide	8,80
C ₁₀ and higher	0,00	Total amount	100,00

* The specific activity of the original butene was 1100 impulses/minute per mg of BaCO₃. In the outgoing gases butene had 244 impulses/minute per mg and butane 22 impulses/minute per mg.

SUMMARY

1. In the synthesis of hydrocarbons and oxygen-containing compounds from CO and H₂ over a fused iron catalyst, butene takes no part in the formation of alcohols and higher (higher than C₉) hydrocarbons and does not act as an intermediate product.
2. Under the conditions studied butene may react with CO and H₂ and give a C₅ hydrocarbon; it undergoes also hydrogenation, oxidation, and hydrocracking.

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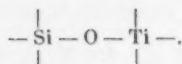
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SYNTHESIS OF SOME (TRIMETHYLSILOXY) TITANIUM COMPOUNDS

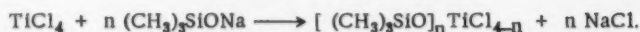
K. A. Andrianov and V. G. Dulova

Progress in the synthesis of polymers having inorganic chains with organic and organosilicon side groups is associated with the development of methods of synthesizing various compounds containing $-Si-O-M-$ groupings. We have succeeded in synthesizing some new compounds containing the grouping



The only known compound of this class was described by English and Sommer [1] in 1955; they synthesized tetrakis(trimethylsiloxy)titanium in 18% yield by the action of titanium tetrachloride on trimethylsilanol. As we have stated previously [2], this compound can be prepared by reaction between $TiCl_4$ and sodium trimethylsiloxide.

We now describe the synthesis of tetrakis(trimethylsiloxy)titanium and of the previously unknown chloro(trimethylsiloxy)titaniums; they were prepared by the following scheme:



We did not succeed in preparing dichlorobis(trimethylsiloxy)titanium by this method, probably because it disproportionates as a result of the catalytic action of impurities, as is sometimes observed [3] in the synthesis of dialkoxydichlorotitaniums. We succeeded in preparing this compound by the action of $TiCl_4$ on tetrakis(trimethylsiloxy)titanium, which is analogous to the synthesis of dialkoxydichlorotitaniums [3].

By the reaction of chlorotris(trimethylsiloxy)titanium with butyl alcohol we obtained butoxytris(trimethylsiloxy)titanium:



This compound is of some interest, for it is the first example of a compound in which titanium is attached simultaneously to alkoxy and siloxy groups. Tetrakis(trimethylsiloxy)titanium is a colorless liquid, stable toward water. When treated with dilute hydrochloric and acetic acids it forms solid polymers. Chloro(trimethylsiloxy)titaniums are crystalline substances that fume strongly in the air. Butoxytris(trimethylsiloxy)titanium is a colorless liquid of ethereal odor which is readily hydrolyzed by water. The isolation and analysis of chloro(trimethylsiloxy)titaniums and butoxytris(trimethylsiloxy)titanium present considerable difficulties. The properties, analyses, and yields of the compounds synthesized are given in the table. The sodium trimethylsiloxide was prepared by the action of sodamide on hexamethyldisiloxane by a previously described method [4].

EXPERIMENTAL

Tetrakis(trimethylsiloxy)titanium. A solution of 0.042 mole of $TiCl_4$ in 40 ml of benzene was added to a stirred cooled (ice water) solution of 0.168 mole of sodium trimethylsiloxide in 85 ml of benzene. The temperature of the mixture did not exceed 30° . When the addition was complete, the mixture was stirred at room temperature for two hours.

After filtration, the tetrakis(trimethylsiloxy)titanium was isolated by vacuum distillation.

Chlorotris(trimethylsiloxy)titanium. Reaction between 0.06 mole of $TiCl_4$ and 0.18 mole of sodium trimethylsiloxide was carried out by the above-described procedure. The chlorotris(trimethylsiloxy)titanium isolated solidified completely after two days in the form of needlelike crystals.

TABLE

Substance	Formula	B.p. in $^{\circ}\text{C}$ (p in mm)	n_D^{20}	d_4^{20}	MR		Yield (%)	Found (%)						Calculated (%)					
					Found	Calc.		C	H	Cl	Si	Ti	C	H	Cl	Si	Ti		
Tetrakis(trimethylsiloxy)titanium	$\text{Ti}[\text{OSi}(\text{CH}_3)_3]_4$	112(11)	1.4277	0.9051	114.66	113.78	66.5	36.72	9.03		27.02	11.93	35.65	8.81		27.71	11.85		
Chlorotris(trimethylsiloxy)titanium	$\text{ClTi}[\text{OSi}(\text{CH}_3)_3]_3$	103-105(10)	—	—	—	—	53.4	31.70	7.15	9.63	25.07	13.84	30.82	7.70	10.12	23.97	13.63		
Dichlorobis(trimethylsiloxy)titanium	$\text{Cl}_2\text{Ti}[\text{OSi}(\text{CH}_3)_3]_2$	72-73(3)	—	—	—	—	80.8	—	—	24.53	18.82	17.81	—	—	23.88	18.86	16.13		
Trichloro(trimethylsiloxy)titanium	$\text{Cl}_3\text{TiOSi}(\text{CH}_3)_3$	67(9)	—	—	—	—	27.3	—	—	44.25	12.50	20.47	—	—	43.71	11.53	19.68		
Butoxytris(trimethylsiloxy)titanium	$\text{C}_4\text{H}_9\text{OTi}[\text{OSi}(\text{CH}_3)_3]_3$	76-77(2)	1.4317	0.9070	111.02	110.71	46.0	40.02	9.61	—	22.70	12.43	40.20	9.27	—	21.69	12.34		

Trichloro(trimethylsiloxy)titanium. This was synthesized under the same conditions from 0.065 mole of TiCl_4 and 0.065 mole of $(\text{CH}_3)_3\text{SiONa}$. In the distillation the trichloro(trimethylsiloxy)titanium solidified in the receiver in the form of large clear crystals.

Dichlorobis(trimethylsiloxy)titanium. With stirring and cooling of the reaction mixture to 5° , a solution of 0.025 mole of TiCl_4 in 8 ml of benzene was added to a solution of 0.025 mole of tetrakis(trimethylsiloxy)titanium in 16 ml of benzene. When the addition was complete, the mixture was stirred at 0° for one hour further, after which the dichlorobis(trimethylsiloxy)titanium was isolated by vacuum distillation. In the course of five days the substance solidified in the form of fine white crystals.

Butoxytris(trimethylsiloxy)titanium. A solution of 0.03 mole of chlorotris(trimethylsiloxy)titanium in 60 ml of benzene was added to a stirred cooled (ice) solution of 0.03 mole of butyl alcohol and 0.03 mole of pyridine in 60 ml of benzene. When the addition was complete, a stream of ammonia was passed into the mixture for two hours. The mixture was stirred at 70° for two hours further, and was then filtered. The butoxytris(trimethylsiloxy)titanium was purified by vacuum distillation. All the syntheses, and also the isolation of the chloro(trimethylsiloxy)titaniums, were carried out with exclusion of atmospheric moisture.

SUMMARY

1. By reaction between TiCl_4 and sodium trimethylsiloxy tetrakis(trimethylsiloxy)titanium, chlorotris(trimethylsiloxy)titanium, and trichloro(trimethylsiloxy)titanium were prepared.

2. Dichlorobis(trimethylsiloxy)titanium was synthesized by the action of TiCl_4 on tetrakis(trimethylsiloxy)titanium.

3. The mixed ester, butoxytris(trimethylsiloxy)titanium, was prepared by the reaction of chlorotris(trimethylsiloxy)titanium, with butyl alcohol.

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CHEMICAL NATURE OF THE WEAK LINKAGES

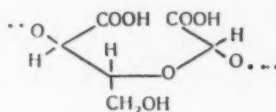
COMMUNICATION 1. EFFECT OF CARBOXY GROUPS IN THE CELLULOSE MOLECULE ON THE STABILITY OF THE GLUCOSIDIC LINK

V. I. Ivanov and Z. I. Kuznetsova

In recent years much attention has been devoted to the study of details of the chemical structure of the cellulose molecule [1], for the known chemical structure of the cellulose molecule [2, 3] cannot explain some of the properties of cellulose, for example the change in the values of hydrolysis constants with time in an acid medium. These investigations were prompted by contemporary practical requirements, which could not be satisfied without clarification of the details of the chemical structure of the cellulose molecule.

From several investigations in this direction it can be seen that in addition to the main glucosidic links there are links which are weaker to the action of acids and alkalis. The chemical nature of these weak bonds has not been unequivocally established. The formation of weak links in the cellulose molecule has been explained first by the biostructure [4] and second by the their formation in the course of the separation of cellulose from accompanying substances as a result of unavoidable oxidative reactions [5, 6]. The reduction in the stability of the cellulose molecule to hydrolysis in an alkaline medium has been associated with the presence of carbonyl groups [7, 8] in the 2-, 3-, and 6-positions.

The reduction of the stability of the cellulose molecule to hydrolysis in an acid medium has been associated with the formation of pentose residues [5] or, on the basis of the work of Jackson and Hudson [9], with the presence in the cellulose molecule of structural units of type (I) [6].



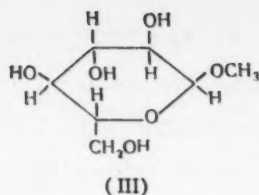
(I)

The formation of such structural units (I) in the molecule of oxidized cellulose, as well as others, has been shown by our investigations. No detailed investigations have been reported concerning the effect of 2- and 3-carboxy groups in the glucose residue on the stability of the glucosidic link in an acid medium.

In this paper we report comparative results on the rate of hydrolysis in an acid medium for a model of oxidized cellulose of structure (I) and a model of unoxidized cellulose; these show that a compound of structure (I) is hydrolyzed 50-60 times as rapidly as a compound containing the usual glucosidic bond.

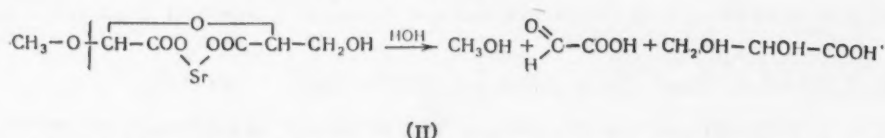
EXPERIMENTAL

As a model of oxidized cellulose we chose D,D'- α -(hydroxymethyl)- α' -methoxydiglycolic acid in the form of its strontium salt (II). As a model of unoxidized cellulose we used methyl α -glucoside (III).



The hydrolysis of (II) and (III) was studied in aqueous 1 N HCl at 60° and 80°. The degree of hydrolysis of methyl α -glucoside was determined from the amount of aldehyde groups formed in the hydrolysis; this was measured by the iodometric method at pH 11 [10].

The hydrolysis of (II) proceeded according to the equation:



which was proved by the isolation of the 2,4-dinitrophenylhydrazine derivate of glyoxylic acid, m.p. 191°. The degree of hydrolysis was determined from the amount of glyoxylic acid formed, which was measured by the iodometric method [11]. Our results show that the strontium salt of D,D'- α -(hydroxymethyl)- α' -methoxydiglycolic acid is hydrolyzed much more rapidly (by a factor of more than 50) than methyl α -glucoside (Tables 1 and 2).

TABLE 1
Hydrolysis of the Strontium Salt of D,D'- α -(Hydroxymethyl)- α' -methoxydiglycolic Acid (0.4% solution) and Methyl α -Glucoside (2% solution) in 1 N HCl at 60°

Sr salt of D, D'- α -(hydroxymethyl)- α' -methoxydiglycolic acid			Methyl α -glucoside			K for Sr salt
Time of hydrolysis (seconds)	Degree of hydrolysis (%)	$K \cdot 10^{-4} \text{ sec}^{-1}$	Time of hydrolysis (seconds)	Degree of hydrolysis (%)	$K \cdot 10^{-6} \text{ sec}^{-1}$	K for methyl α -glucoside
600	13,09	2,415	2	2,87	3,227	79
1200	21,70	2,040	4	3,42	2,405	
1800	34,15	2,322	6	4,78	2,381	
3600	56,48	2,322	8	5,96	2,135	
			10	7,408	2,143	
Average value of $K = 2,27 \cdot 10^{-4} \text{ sec}^{-1}$			Average value of $K = 2,85 \cdot 10^{-6} \text{ sec}^{-1}$			

TABLE 2
Hydrolysis of the Strontium Salt of D,D'- α -(Hydroxymethyl)- α' -methoxydiglycolic Acid (0.4% solution) and Methyl α -Glucoside (2% solution) in 1 N HCl at 80°

Sr salt of D, D'- α -(hydroxymethyl)- α' -methoxydiglycolic acid			Methyl α -glucoside			K for Sr salt
Time of hydrolysis (seconds)	Degree of hydrolysis (%)	$K \cdot 10^{-3} \text{ sec}^{-1}$	Time of hydrolysis (seconds)	Degree of hydrolysis (%)	$K \cdot 10^{-5} \text{ sec}^{-1}$	K for methyl α -glucoside
150	22,54	1,704	1	9,49	2,440	57
300	39,15	1,656	2	17,06	2,610	
450	41,77	1,201	3	22,81	2,310	
600	56,87	1,402	4	25,42	2,040	
900	66,76	1,100	5	35,72	2,440	
			6	42,02	2,520	
Average value of $K = 1,412 \cdot 10^{-3} \text{ sec}^{-1}$			Average value of $K = 2,46 \cdot 10^{-5} \text{ sec}^{-1}$			

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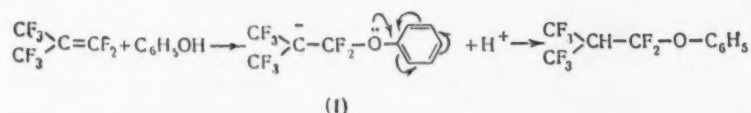
** In Russian.

REACTIONS OF SOME FLUORO OLEFINS WITH PHENOLS

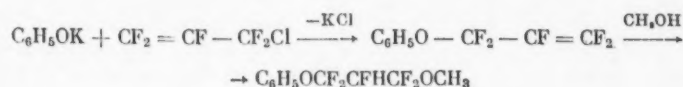
I. L. Knuniants and B. L. Diatkin

The specific character of the double bond in perfluoroisobutene and perfluoroacrylonitrile is particularly manifested in the exceptional reactivity of these compounds toward nucleophilic reagents. Thus, alcohols add in absence of alkaline catalysts and without the application of heat [1-4], and in the case of perfluoroisobutene a vinyl fluorine atom can be replaced by an alkoxy group [2, 3]. It was considered to be of interest to study the behavior of these fluoro olefins toward phenols, in which, because of the withdrawal of the electron pair of the oxygen by the aryl radical, the nucleophilic character of the molecule and corresponding anion is considerably weaker than in the case of alcohols.

It was found that perfluoroisobutene and perfluoroacrylonitrile combine with phenol and hydroquinone without alkaline catalysts when heated in an autoclave to 100-120°; the liberation of hydrogen fluoride and formation of substitution products were noted. It is probable that the degree of mobility of the free electron pair on the oxygen is insufficient here for the activation of the fluorine in the α -position and the intermediate ion (I) is stabilized only by the capture of a proton:



We also carried out the reactions of perfluoroallyl chloride and perfluoroallyl iodide with potassium phenoxide. Replacement of halogen in the allyl position by phenoxy occurred with formation of perfluoroallyl phenyl ether, the structure of which was confirmed by the addition of methanol at the double bond:



In a quite analogous way, methanol adds to methyl perfluoroallyl ether with formation of 1,1,2,3,3-pentafluoro-1,3-dimethoxypropane, which was converted by hydrolysis into derivatives of fluoromalonic acid. Unlike its alkyl analogs, perfluoroallyl phenyl ether does not undergo the allyl rearrangement when kept for a long time or heated. This fact is in accord with a suggestion that we made previously, namely, that the tendency for substituted perfluoropropenes to undergo allyl rearrangement is determined by the mobility of the free electron pair of the substituent [5].

EXPERIMENTAL

Addition of Phenols to Perfluoroisobutene and Perfluoroacrylonitrile. A mixture of the phenol and fluoro olefin (molar ratio 1 : 1.5) was heated in an autoclave at 100-120° for 15 hours; the excess of olefin was driven

TABLE
Addition of Phenols and Hydroquinones to Perfluoroisobutene and Perfluoroacrylonitrile

No.	Formula of substance	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Found (%)			Calculated (%)		
						found	calculated	C	H	F	C	H	F
1	$C_6H_5OCF_2CH(CF_3)_2$	85	68, 5 (20)	1,3900	1,4534	47,98	47,54	40,80	2,12	59,40	40,83	2,06	59,58
2	$n-C_6H_4(OCF_2CH(CF_3)_2)_2$	72	109-110 (10)	1,3600	1,6357	68,84	68,78	54,35	0,90	27,83	32,95	1,18	28,33
3	$C_6H_5OCF_2CFHCN$	87	76 (7)	1,4490	1,2594	42,84	42,04	45,77	2,72		53,73	3,00	
4	$n-C_6H_4(OCF_2CFHCN)_2$	76	139, 5-140 (4)	1,4426	1,4209				1,86		44,45	1,87	

off, and the reaction product was vacuum-distilled. The yields, physical properties, and results of the analyses of the compounds obtained are given in the table.

Perfluoroallyl Phenyl Ether. A mixture of 5.6 g of KOH, 9.4 g of C_6H_5OH , and 30 ml of water was added dropwise over a period of 3.5 hours to a stirred solution of 40 g of the chloropentafluoropropene fraction from the pyrolysis of $CF_2 = CFCI$ (a mixture of $CF_2 = CF - CF_2Cl$ and $CF_2 = CCl - CF_3$ in 50 ml of dioxane at room temperature. Stirring at room temperature was continued for one hour, the excess of olefin was then driven off, the mixture was poured into water, and the oil that separated was dried over $CaCl_2$ and vacuum distilled. The product, amounting to 6.9 g (32.2%), was perfluoroallyl phenyl ether, b.p. 54-57° (20 mm) and n_D^{20} 1.4201. After redistillation it had b.p. 54° (20 mm), n_D^{20} 1.4190; d_4^{20} 1.3467. Found MR 42.03; calculated for $C_9H_5F_5O$ 4 F MR 42.04. By the use of $CF_2 = CF - CF_2I$ a yield of 42.8% can be obtained.

Found %: C 48.22 H 2.48 $C_9H_5F_5O$. Calculated %: C 48.23; H 2.25.

Addition of Methanol to Perfluoroallyl Phenyl Ether. A solution of 6.7 g of perfluoroallyl phenyl ether in 5 ml of methanol was added dropwise to a stirred cooled solution of 1.5 g of KOH in 10 ml of methanol. After several hours the mixture was poured into water and extracted with ether; the ether extract was washed with water and dried over $MgSO_4$. Ether was distilled off, and distillation of the residue gave 4 g (52.4%) of 1,1,2,3,3-pentafluoro-1-methoxy-3-phenoxypropane, b.p. 86-91° (7 mm). After redistillation it had b.p. 85-86° (7 mm); n_D^{20} 1.4219; n_D^{20} 1.3420; found MR 48.50; Calculated for $C_{10}H_5F_5O_2$ 3 F MR 48.76.

Found %: C 46.57; H 3.35 $C_{10}H_5F_5O_2$. Calculated %: C 46.88, H 3.54.

Addition of Methanol to Methyl Perfluoroallyl Ether. A mixture of 15 g of methyl perfluoroallyl ether [5] and 20 ml of methanol was added dropwise to a stirred cooled solution of sodium methoxide (2.3 g of Na in 50 ml of methanol). The further treatment was as in the preceding experiment. The product, amounting to 9 g (50%), was 1,1,2,3,3-pentafluoro-1,3-dimethoxypropane; b.p. 64-65° (110 mm); n_D^{20} 1.3330; d_4^{20} 1.3673; found MR 29.20; calculated for $C_5H_7F_5O_2$ MR 29.28.

Found %: C 30.92; H 3.49 $C_5H_7F_5O_2$. Calculated %: C 30.94; H 3.63.

A little of the pentafluorodimethoxypropane was treated with concentrated H_2SO_4 , washed with water, and subjected to the action of concentrated ammonia; fluoromalonamide, m.p. 199-200° (from water), was obtained.

Found %: C 30.28; H 4.44 $C_3H_5FO_2N_2$. Calculated %: C 30.00; H 4.20.

SUMMARY

1. The noncatalytic additions of phenol and of hydroquinone to perfluoroisobutene and to perfluoroacrylonitrile were carried out.
2. By the action of potassium phenoxide on perfluoroallyl chloride, perfluoroallyl phenyl ether was prepared.

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NEW METHOD OF PREPARING GRAFT COPOLYMERS

With the object of modifying the properties of heterochain polyamides we searched for a method of grafting a layer of a carbon-chain polymer to the surface of the polyamide. As a result of this search we found a method of obtaining such a layer of graft copolymer on the surface of a heterochain polyamide. This method consists in the preliminary formation of peroxide groups on the polyamide surface, and these then initiate the formation of grafted macromolecules of carbon-chain polymer in these places. For this purpose the most successful agent was found to be ozone.

Polyamide films were treated with ozone and then with a vinyl monomer. As a result of such treatment a layer of polystyrene or other polymer was formed on the surface of the polyamide film, and this layer was firmly attached to the polyamide and could not be removed by treatment with boiling benzene or other solvent for many hours. The thickness and weight of grafted polymer depends on the duration of the ozone treatment. In our experiments the increase in the weight of the film varied in the range 4.0-20.0%. The mechanical properties of the film varied in greater or lesser degree according to the conditions and duration of the treatment.

This method of preparing graft copolymers of polyamides with carbon-chain polymers has been found to be suitable in the case of such heterochain polyamides as polycaprolactam and the mixed polyamide Anid G-669, and also in the case of polyesters such as polyethylene terephthalate (Lavsan).

V. V. Korshak and K. K. Mozgova

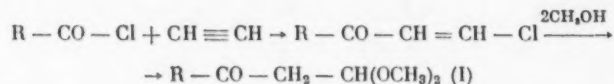
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CHEMICAL CONFERENCE IN THE GERMAN FEDERAL REPUBLIC
IN 1957

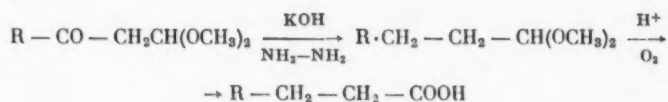
II. Annual Meeting of the German Society for the Investigation of Fats. On October 13-18, 1957, immediately after the meeting of the Society for the Chemistry of Petroleum and Coal, the Annual Meeting of the German Society for the Investigation of Fats (president Prof. Kaufmann) was held, also in West Berlin. This closeness in time and place of conferences of scientific societies so closely allied in fields of interest cannot but be regarded as most fortunate. The following papers were read at the plenary session: 1) H. P. Kaufmann (Munster), "New Syntheses from Fatty Acids and Glycerides", 2) A. Seger (Munster), "Reactions of Addition to Alkyne Acids", 3) K. E. Schulte (Berlin), "Properties of Alkyne Acids", 4) A. Rieche (Berlin), "Significance of Organic Peroxides in the Chemistry of Fats", 5) A. D. Petrov (Moscow), "Synthesis of Fatty Esters of High Molecular Weight by the Telomerization of Formic Esters with Olefins", 6) H. P. Kaufmann (Munster), "New Methods for the Qualitative and Quantitative Analysis of Fats by Paper Chromatography", and 6) L. Oda (Kyoto), "Synthesis of New Surface-active Agents". Owing to lack of space we shall discuss only the first and last papers.

H. P. Kaufmann and W. Stamm studied methods of preparing the acid chlorides of nonanoic and higher fatty acids, and also the addition of these to acetylene with formation of alkyl 2-chlorovinyl ketones (alkyl 2-chlorovinyl ketones of lower molecular weight were synthesized earlier by A. N. Nesmeianov and N. K. Kochetkov). From alkyl 2-chlorovinyl ketones it is easy to pass to β -keto acetals (I):

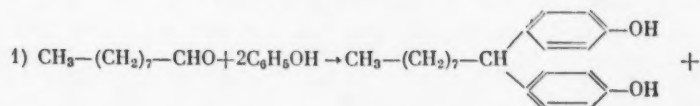


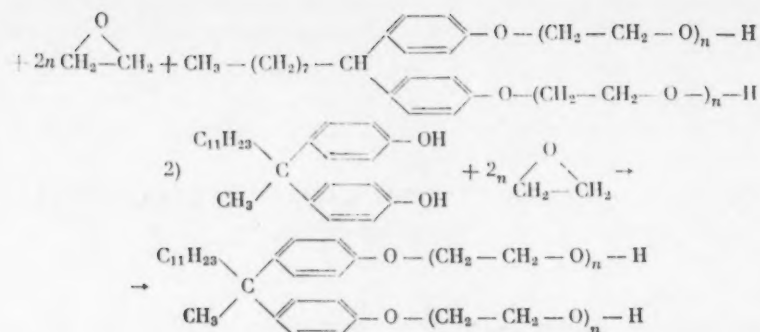
β -Keto acetals of medium molecular weight (C_9 - C_{12}), which smell like oranges, have been proposed for use in cosmetics and soap perfumery.

From β -keto acetals it is not difficult (e.g. by the action of KOH and NH_2NH_2) to pass to acids containing two more carbon atoms in the chain:



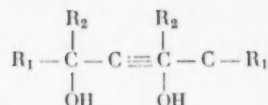
As is well known, by the condensation of alkylphenols with ethylene oxide an important type of compound can be synthesized, namely the so-called nonionic detergents. Diphenols, which were first synthesized by the condensation of two phenol molecules with a molecule of aldehyde or ketone by A. P. Dianin, are now widely available. Oda selected aldehydes and ketones having a fairly long alkyl chain, condensed them with phenols, and obtained diphenols which gave new nonionic detergents when condensed with ethylene oxide. Nonanal was prepared by him by the oxidation of oleic acid, and 2-tridecanone from an equimolecular mixture of acetic and undecanoic acids:



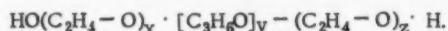


In the sectional sessions — a) soaps and detergents; b) paints and waxes; c) biology of edible fats; d) material resources for fats — more than 50 papers were read, and these will be published in "Fette, Seifen, Anstrichmittel". We can list here only a few of these papers: 1) A. Metzger (Kempten), "Properties of Branched Fatty Acids"; 2) J. Stawiz (Wiesbaden), "Mechanism of the Action of Carboxymethylcellulose"; 3) W. Witke, "Unsaturated Polyester Resins and their Importance in the Paint Industry"; 4) D. Russman (U.K.), "Action of γ -Rays on Fats"; 5) R. Auerbach (Berlin), "Lines of Development in Atomic Physics"; 6) F. Karrier (Holland), "Structural Principles of Detergents"; 7) Papers from the laboratory of Academician W. Bertsch (German Democratic Republic), i.e. a) H. Linde, "Diffusion and Convection Phenomena in presence of Surface-active Agents"; b) E. Ulperger, "Synthesis of Surface-active Agents from Carbohydrates"; 8) K. Teufel (Potsdam), "Detection of Traces of Metals in Fats by Emission Spectrography"; 9) K. Wullenweber (Hamburg), "Epoxy Resins Modified with Alkyd Resins"; 10) G. Schiemann (Hanover), "Styrenized Paints"; 11) K. Ledwoch (Hamburg), "Paints based on Melamine Ethers".

Of these papers, that of Karrier is interesting in that it mentions two new kinds of detergents. One of these is a ditertiary acetylenic glycol:



in which $\text{R}_1 = \text{C}_4$ and $\text{R}_2 = \text{C}_2, \text{C}_3$, or phenyl. As is known, this kind of glycol is readily synthesized by the condensation of acetylene with ketones having radicals larger than CH_3 under pressure in presence of KOH in a nonester medium. Such products are manufactured under the name of Surfinols by the Air Reduction Chemical Company, N. J. Products of the second type (Pluronics) are prepared by the Wyandotte Chemical Company of Michigan, U. S. A., by the addition of ethylene oxide to the condensation product from propylene oxide and 1,2-propanediol:



It is interesting to note that, whereas most surface-active agents have molecular weights of 300-500 (Surfinols even 170-230), Pluronics have molecular weights in the range 2000-7500.

Already from the simple enumeration of the papers it will be seen that the German chemical industry pays great attention to investigations on the synthesis of new kinds of detergents and also of new kinds of paints capable of replacing scarce linseed oil and tropical resins. It is interesting also to note that, whereas at the first conference, which was devoted to the chemistry of hydrocarbons, much attention was given to the action of nuclear radiations on hydrocarbons, we here meet papers on the action of the same radiations on fats.

There were many representatives of the People's Democracies present who did not read papers at the conference. We found great interest in conversations with some of these (Academician Berg (German Democratic Republic), Academician M. Freund (Budapest), Professor G. Newiadomski (Gdansk, Poland)). Also, by meeting

the president of the Society, Prof. Kaufmann, who had been invited by the Academy of Sciences of the USSR to read papers in Moscow and Leningrad, we were able to arrange about the subjects of his papers and the time of his visit.

At the end of the conference we took part in an excursion to a works of the firm of Schering at which hormone preparations were manufactured. Later, at the invitation of Academician Bertsch, we inspected his laboratory at Adlershof (East Berlin) on our way home.

A. D. Petrov, N. I. Shulkin

ERRATA

Number 2, February 1958

Page	Line	Reads	Should read
146	6	2-Bromo-3-chlorovaleric Acid	2-Bromo-5-chlorovaleric Acid
	8	2-bromo-3-chlorovaleric acid	2-bromo-3-chlorovaleric Acid

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.



